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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

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SILICATES OF THE RARE EARTH ELEMENTS

COMMUNICATION 2. PHASE DIAGRAM OF THE BINARY SYSTEM

GADOLINIUM OXIDE - SILICA

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In [1, 2] one of the authors together with Bondar carried out the first synthesis of the lanthanum silicate $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, described its properties, and established the range of eliquation into the La_2O_3 - SiO_2 system. In a short communication Glasser, Warshaw, and Roy [3], and also Warshaw and Roy [4], stated that they had studied the phase equilibria in the binary systems of silica with rare earth oxides and had synthesized compounds with compositions $\text{Ln}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{Ln}_2\text{O}_3 \cdot 2\text{SiO}_2$. According to Curtis and Johnson [5] gadolinium oxide after being heated at temperatures below 1300° has a cubic structure; its theoretical density is 7.407. After being heated at 1300° it is anisotropic and has refractive index $n = 1.82$; its structure was not established.

Experimental Part

Gadolinium oxide (98.2%), with total content of other rare earth elements equal to 1.75%, and powdered rock crystal (99.90% SiO_2) were used for preparation of the specimens. The specimens were prepared in small, 0.5 g, portions. The weighed portions of the oxides were ground together for a long time in the agate mortar and compressed into the form of small cylinders.

The method of firing and annealing was studied with variations in the experimental details. In order to determine the liquidus temperature of the rapidly crystallizable specimens they were heated to complete fusion in a vacuum microfurnace, and then the temperature was further raised by approximately 200° . Thereupon the soaking temperature, which was maintained for not more than one minute, was established, and the specimens became annealed. In order to establish the temperatures of invariant changes in the solid state, or of reactions proceeding at temperatures lying below the liquidus, prolonged soaking, amounting to ten hours at 1600° (platinum furnace), was used. In this case both fused specimens and specimens which had not been preliminarily fused were used. By such means reactions occurred at the soaking temperature between the crystallization products, which were compounds of the components of the system, and also between the free oxides. The fired products were studied under a microscope in immersion media and in cross-sectional view. Phosphoric immersion media were used for determination of the refractive indices of the mineral systems having the constants in question greater than 1.75. Phase identification was also carried out by means of X-ray analysis. The x-ray diffraction data were obtained in a Debye chamber and in an ionization chamber.

The phase diagram of the Gd_2O_3 - SiO_2 system, plotted from the results of the current investigation, is shown in Fig. 1. The existence of three compounds with compositions $\text{Gd}_2\text{O}_3 \cdot \text{SiO}_2$, $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$, and $\text{Gd}_2\text{O}_3 \cdot 2\text{SiO}_2$ was established. There are two maxima on the liquidus curve, corresponding to the fused compounds $\text{Gd}_2\text{O}_3 \cdot \text{SiO}_2$ and $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$, and three eutectics: one is between Gd_2O_3 and $\text{Gd}_2\text{O}_3 \cdot \text{SiO}_2$, another is between $\text{Gd}_2\text{O}_3 \cdot \text{SiO}_2$ and $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$, and the third is between $\text{Gd}_2\text{O}_3 \cdot 2\text{SiO}_2$ and SiO_2 . There is a large separation zone in the diagram. The liquidus curve was plotted from the firing and annealing experimental results given in Table 1.

Gadolinium oxide, Gd_2O_3 , melts at 2200° . This temperature is 150° lower than that determined by Curtis and Johnson. The melting point was established in a microfurnace having a tungsten heating element. The Gd_2O_3 was compressed into the form of a small stick and was suspended vertically, on molybdenum wire, in the furnace. The free end of the stick was located in the center of the hot zone of the spiral heating element, and the temperature at which it started to melt was taken to be the melting point.

TABLE 1. Annealing of Specimens of the $Gd_2O_3-SiO_2$ System

Composition (wt. %)		Soaking temp. (°C)	Duration	Phase*
Gd_2O_3	SiO_2			
95	5	2050	10 sec.	Glass
		2000	15 »	Gd_2O_3 + glass
92,5	7,5	1850	30 »	Glass
		1800	30 »	Gd_2O_3 + secondary fine crystals
				$2Gd_2O_3 \cdot 3SiO_2$ + glass
90	10	1900	30 »	Glass
		1850	30 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass
		1800	30 »	$2Gd_2O_3 \cdot 3SiO_2$ + secondary fine crystals
				Gd_2O_3 + glass
85,8	14,2	2000	15 »	Glass
		1900	15 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass (very little)
82	18	1900	30 »	Glass
		1800	30 »	$Gd_2O_3 \cdot SiO_2$ + $2Gd_2O_3 \cdot 3SiO_2$
80	20	2000	15 »	Glass
		1950	15 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass (very little)
77	23	1950	15 »	Glass
		1850	15 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass
75	25	1900	15 »	Glass
		1870	30 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass
70	30	1750	3 min.	Glass
		1700	3 »	$2Gd_2O_3 \cdot 3SiO_2$ + glass
67,5	32,5	1650	5 »	Glass
		1550	5 »	Eutectic crystallization of $Gd_2O_3 \cdot 2SiO_2$ + cristobalite
65	35	1800	1 »	Glass
		1750	2 »	Two glasses
		1700	10 »	Cristobalite + glass
		1630	15 »	Cristobalite + $Gd_2O_3 \cdot 2SiO_2$
60	40	1900	30 sec.	Glass
		1800	1 min.	Two glasses
		1750	5 »	Two glasses
		1700	30 »	Cristobalite + glass
		1600	2 hours	Cristobalite + $Gd_2O_3 \cdot 2SiO_2$

*In most of the compounds by "glass" is meant a mixture of glass and fine crystals which separates out during the annealing process.

TABLE 2. X-ray Investigation of Compounds of the $Gd_2O_3-SiO_2$ System

$Gd_2O_3 \cdot SiO_2$		$2Gd_2O_3 \cdot 3SiO_2$		$Gd_2O_3 \cdot 2SiO_2$		$Gd_2O_3 \cdot SiO_2$		$2Gd_2O_3 \cdot 3SiO_2$		$Gd_2O_3 \cdot 2SiO_2$	
d/n	I/I_0	d/n	I/I_0	d/n	I/I_0	d/n	I/I_0	d/n	I/I_0	d/n	I/I_0
4,43	24	4,08	38	4,09	40	1,72	33	2,11	52	1,78	43
4,19	20	3,44	31	3,47	64	1,62	22	1,94	26	1,70	51
3,98	18	3,23	62	3,34	20	1,53	24	1,82	12	1,67	77
3,21	33	3,11	31	3,21	29	1,50	24	1,84	48	1,65	39
3,14	67	2,90	69	3,27	40	1,47	22	1,79	33	1,60	40
2,93	75	2,81	36	3,14	28	1,45	20	1,75	21	1,55	49
2,83	100	2,75	69	2,91	57	1,42	20	1,69	40	1,53	55
2,80	85	2,65	33	2,75	88	1,32	18	1,67	43	1,47	80
2,75	59	2,52	31	2,66	34	1,24	26	1,55	33	1,41	57
1,99	24	2,48	71	2,55	26	1,22	18	1,47	52	1,27	51
1,95	28	2,46	48	2,49	65			1,46	52	1,17	29
1,90	33	2,37	52	2,31	100			1,41	43		
1,84	47	2,31	100	2,10	31			1,27	36		
1,82	22	2,24	52	1,97	20			1,23	21		
1,78	43	2,21	31	1,87	47			1,17	33		
1,76	43	2,16	24	1,85	61						

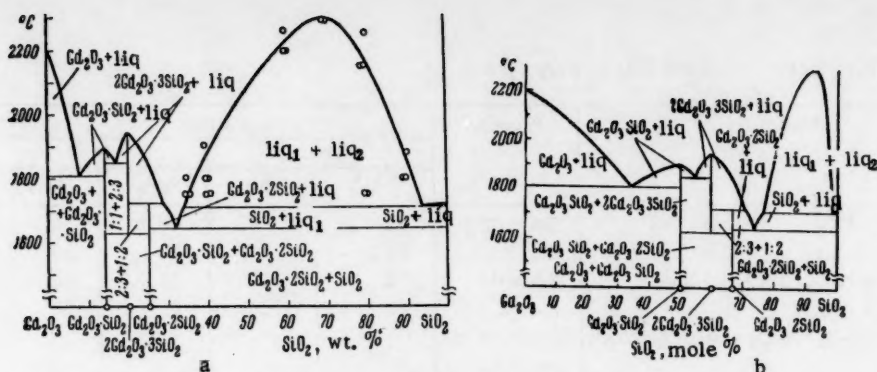


Fig. 1. Phase diagram of the $Gd_2O_3-SiO_2$ system: A) In wt. %; B) in mole %.

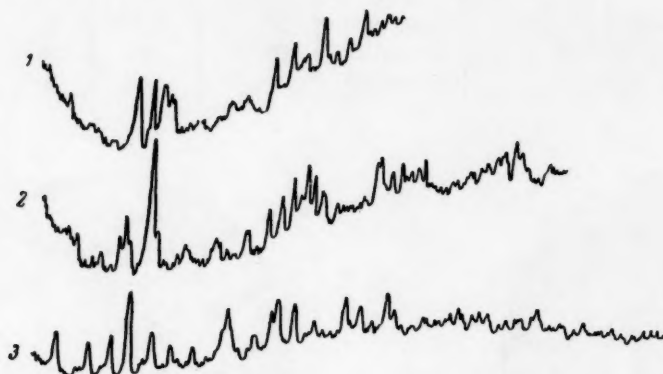


Fig. 2. X-ray diffraction curves of compounds of the $Gd_2O_3-SiO_2$ system: 1) $Gd_2O_3 \cdot SiO_2$; 2) $2Gd_2O_3 \cdot 3SiO_2$; 3) $Gd_2O_3 \cdot 2SiO_2$.

The refractive index of Gd_2O_3 after heating at 1000° is $n = 1.91$; the compound fused in an arc has $n_g = 2.035$, $n_p = 2.010$, $n_g - n_p = 0.025$. The crystals are biaxial, negative. The X-ray diffraction data for gadolinium oxide, fired at 1000° and fused in an arc, agreed with Curtis and Johnson's X-ray data. The only observed difference was in the intensities of the lines. In particular, the Curtis and Johnson compound heated at 1300° had a more intense line corresponding to the interplanar distance $d = 2.75$, whereas our compound fused in an arc had a more intense line corresponding to $d = 2.96$. The cited difference is evidently connected with the different thermal treatment.

The compound $Gd_2O_3 \cdot SiO_2$ melts without decomposition at 1900° ; its optical constants are $n_g = 1.890$, $n_p = 1.873$, $n_g - n_p = 0.017$. The crystals are biaxial, positive, with a large optic axial angle of the order of 75° ; density 6.552. The X-ray diffraction curves (Fig. 2) were obtained from two specimens having initial molar compositions 1:1; one of these was produced by heating the oxide mixture at 1600° for two hours and the other was produced by fusion in a microfurnace. The X-ray diffraction curves, and also the optical data, indicate that one and the same compound was formed. The calculated interplanar distances are shown in Table 2. Well developed crystals of this compound (Fig. 3) were produced from a melt containing excess gadolinium oxide.

The compound $2Gd_2O_3 \cdot 3SiO_2$ is stable only in the temperature range $1630-1950^\circ$. At 1950° this compound melts without decomposition. Below 1630° it decomposes into two other compounds, $Gd_2O_3 \cdot SiO_2$ and $Gd_2O_3 \cdot 2SiO_2$. The interplanar distances (Table 2) were calculated from the X-ray diffraction curve (Fig. 2) obtained from a specimen having molar composition 2:3 which had been fused in a microfurnace and rapidly cooled. An X-ray diffraction curve of a specimen having the same composition, but produced by sintering the oxides at 1600° for ten hours, comprised only the lines of two other compounds, 1:1 and 1:2. The results of the microscopic determination of the phase composition of fused and sintered specimens agreed in all respects with the X-ray analysis data. The optical

constants of the $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ compound are $n_o = 1.870$, $n_e = 1.855$, $n_o - n_e = 0.015$; the crystals are uniaxial, hexagonal, of negative sign, with parallel extinction; density 6.290. A microphotograph of $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ crystals is shown in Fig. 4.

TABLE 3. Invariant Points in the Gd_2O_3 - SiO_2 System

Phases	Process	Composition				Temp. (°C)
		Wt. %		Mole %		
		Gd ₂ O ₃	SiO ₂	Gd ₂ O ₃	SiO ₂	
Gd ₂ O ₃ + Gd ₂ O ₃ · SiO ₂ + liquid	Eutectic	92	8	65.7	34.3	1810
Gd ₂ O ₃ · SiO ₂ + liquid	Fusion	85.8	14.2	50	50	1900
Gd ₂ O ₃ · SiO ₂ + 2Gd ₂ O ₃ · 3SiO ₂ + liquid	Eutectic	83	17	45	55	1850
2Gd ₂ O ₃ · 3SiO ₂ + liquid	Fusion	80	20	40	60	1950
Gd ₂ O ₃ · SiO ₂ + Gd ₂ O ₃ · 2SiO ₂ + 2Gd ₂ O ₃ · 3SiO ₂	Reaction in the solid state	80	20	40	60	1630
2Gd ₂ O ₃ · 3SiO ₂ + Gd ₂ O ₃ · 2SiO ₂ + liquid	Incongruent fusion	71	29	29	71	1720
Gd ₂ O ₃ · 2SiO ₂ + α-cristobalite + liquid	Eutectic	68	32	26.4	73.6	1640
α-cristobalite + liquid A + liquid B	Eliquation	66	34	24.4	75.6	1710
α-cristobalite + liquid A + liquid F	Eliquation	5	95	1	99	1710



Fig. 3. $\text{Gd}_2\text{O}_3 \cdot \text{SiO}_2$ crystals.



Fig. 4. $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ crystals.

The compound $\text{Gd}_2\text{O}_3 \cdot 2\text{SiO}_2$ melts at 1720° with decomposition into $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ and liquid; its optical constants are $n_g = 1.775$, $n_p = 1.765$, $n_g - n_p = 0.010$; the crystals are biaxial, of positive sign, with parallel extinction; density 5.336. The X-ray diffraction curve (Fig. 2) interplanar distances, calculated for a specimen fired at 1600° for ten hours, are given in Table 2.

Primary partially resorbed $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ crystals and secondary elongated $\text{Gd}_2\text{O}_3 \cdot 2\text{SiO}_2$ crystals (annealed) at 1850° can be seen in the microphotograph (Fig. 5). Separation of the melt begins at 1710° . At this temperature two liquids coexist, one of which has the composition 65% Gd_2O_3 and 35% SiO_2 , and the other has the composition approximately 5% Gd_2O_3 and 95% SiO_2 . The upper crystal point of the separation zone lies at 2300° ; its composition is 30% Gd_2O_3 and 70% SiO_2 .

The invariant point compositions and temperatures for the Gd_2O_3 - SiO_2 system are given in Table 3.



Fig. 5. Primary resorption crystals of $2\text{Gd}_2\text{O}_3 \cdot 3\text{SiO}_2$ and secondary crystals of $\text{Gd}_2\text{O}_3 \cdot 2\text{SiO}_2$.

SUMMARY

1. The phase diagram of the binary system $\text{Gd}_2\text{O}_3\text{--SiO}_2$ was studied and constructed.

2. Compounds of the types oxyorthosilicate ($\text{Gd}_2\text{O}[\text{SiO}_4]$), orthosilicate ($\text{Gd}_4[\text{SiO}_4]_3$), and pyrosilicate ($\text{Gd}_2\text{Si}_2\text{O}_7$) were synthesized. The properties of these compounds were studied.

3. The limits of the eliquation zone were established and its upper crystalline point was determined.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SILICATES OF THE RARE EARTH ELEMENTS

COMMUNICATION 3. PHASE DIAGRAM OF THE BINARY SYSTEM

YTTRIUM OXIDE - SILICA

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As we showed earlier [1, 2], the study of the rare earth elements, their oxides, and their other compounds is growing both in the Soviet Union and abroad. Recently works have appeared in the literature describing the study of the ceramic properties of the oxides of such rare earth elements as yttrium, samarium, gadolinium, dysprosium, and europium [3-5], and also describing the study of the reaction products of gadolinium and samarium oxides with alumina and the utilization of these products as ceramic materials [6]. A short note by Roy [7] is all that has appeared in connection with the study of the silicates of the rare earth elements. The author describes a study of the phase equilibria in a series of Ln_2O_3 - SiO_2 systems in silica-rich regions ($\text{Ln} = \text{La, Nd, Dy, Gd, Eu, Yb, Y}$), without giving the phase diagrams. An immiscibility zone and two types of chemical compounds, $\text{Ln}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{Ln}_2\text{O}_3 \cdot 2\text{SiO}_2$, were discovered in the cited systems. Natural silicates of the rare earth elements which are known are minerals which contain yttrium: thortveitite ($(\text{Sc, Y})_2\text{Si}_2\text{O}_7$), yttrialite ($(\text{Y, Th})_2\text{Si}_2\text{O}_7$), and thalenite ($\text{Y}_2\text{Si}_2\text{O}_7$). The largest amount of yttrium is contained in thalenite (approximately 47.5%). In these minerals Fe_2O_3 , CaO , MgO , ThO_2 , Al_2O_3 , etc. are found as impurities. Thalenite occurs with fergusonite, cyrtolite, and gadolinite in Norwegian and Swedish granite pegmatite. According to Sjögren [8] and Vogt [9], thalenite crystals belong to the monoclinic syngony, are biaxial, negative, have large optic axial angles ($2V = 68^\circ$), have refractive indices $n_g = 1.7436$, $n_m = 1.7375$, $n_p = 1.7312$, and birefringence $0.012 (n_g - n_p)$. The construction of the phase diagram for the Y_2O_3 - SiO_2 system was the object of our work.

Experimental Part

The method used by us in order to study phase equilibria in various systems has been described repeatedly [10, 11]. In the current work the following raw materials were used for preparation of the specimens: silica (99.90% SiO_2) and yttrium oxide (total rare earth oxide (99.9%, yttrium oxide content 99.42%, total rare earth oxide other than yttrium oxide 0.55%, calcium 0.02%, iron <0.01%, and copper 0.05%). Specimens were prepared by prolonged grinding of the oxide mixture in an agate mortar, forming into a small stick with dextrin solution, sintering at 1100° , and fusion in an oxyhydrogen flame or an electric arc.

Another method of producing specimens consisted of compressing a carefully blended oxide mixture into small tables. The specimens produced by this and the other method were subjected to firing and annealing. The annealing was accomplished in a high-temperature vacuum microfurnace in a stream of argon. The specimen was heated to 150 - 200° above its melting point, then the temperature was reduced to a fixed amount at which the specimen was held for a fixed time, after which it was removed from the hot zone of the furnace with the aid of a magnet. The duration of the soaking before annealing varied from 30 sec to 5-15 min. In the latter case, with prolonged soaking, the specimens were enveloped with tungsten in order to prevent change in composition, and only after this was it exposed to the appropriate thermal treatment. For comparatively low temperatures (1600° and below) a furnace with a platinum-rhodium heating element, in which the specimens were annealed for up to ten hours, was used.

The products were studied microscopically (immersion media, thin sections, and cross-sections) and by X-ray structure analysis; in some cases chemical analysis was used. Phosphoric immersion liquids were used in order to determine the refractive indices of the highly refractive materials.

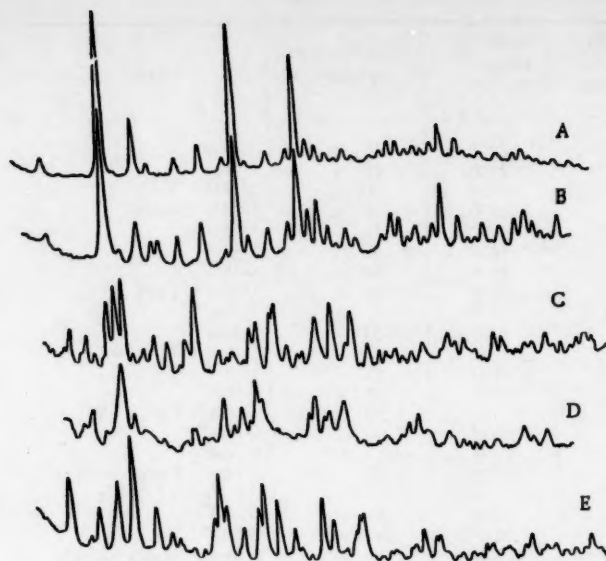


Fig. 1. X-ray diffraction curves of the specimens: A) Yttrium oxide fired at 900° for two hours; B) yttrium oxide fused in an electric arc; C) yttrium oxyorthosilicate, $Y_2O[SiO_4]$ or $Y_2O_3 \cdot SiO_2$; D) yttrium orthosilicate, $Y_4[SiO_4]_3$ or $2Y_2O_3 \cdot 3SiO_2$; E) yttrium pyrosilicate, $Y_2[SiO_7]$ or $Y_2O_3 \cdot 2SiO_2$.

TABLE 1. X-ray Investigation of Yttrium Oxide (Fired at 900°)

Our data		Swanson's data [12]		Our data		Swanson's data [12]	
d/n	I/I_0	d/n	I/I_0	d/n	I/I_0	d/n	I/I_0
4,34	11	4,34	16	1,371	4	1,470	1
3,07	100	3,06	100	1,346	8	1,443	3
2,654	41	2,652	30	1,326	11	1,417	2
2,503	9	2,500	7	1,307	10	1,346	2
2,263	11	2,372	1	1,286	6	1,325	4
2,083	13	2,261	8	1,268	6	1,305	3
1,939	10	2,165	1	1,250	4	1,287	1
1,878	71	2,080	12	1,233	10	1,267	2
1,822	5	1,874	46	1,217	13	1,249	1
1,723	11	1,818	2	1,186	12	1,233	3
1,637	10	1,769	1	1,172	5	1,216	8
1,600	55	1,720	5	1,158	4	1,185	5
1,565	14	1,677	1	1,144	4	1,170	1
1,532	11	1,636	4	1,119	5	1,157	1
1,499	6	1,599	31	1,095	4	1,143	2
1,472	4	1,563	7	1,083	8	1,117	2
1,445	8	1,531	5	1,072	3	1,093	2
1,418	5	1,499	2	1,041	4	1,082	5

It is known from the literature [3] that Y_2O_3 melts at 2410° and has refractive index $n = 1.91$. Yttrium oxide fired at 900° for two hours, in conformity with our data, is a crystalline powder, isotropic under the microscope, with refractive index $n = 1.90$. An X-ray diffraction curve of such a product, obtained with the aid of an ionization chamber, is shown in Fig. 1,A, and the data calculated from it is given in Table 1.

TABLE 2. Results of Annealing the Specimens

Comp. (wt. %)		Soaking temp. (°C)	Duration of soaking	Phase
Y ₂ O ₃	SiO ₂			
95	5	2200	15 sec	Glass*
		2100	15 »	Glass*
		2050	30 »	Glass + Y ₂ O ₃
		2000	30 »	Glass + Y ₂ O ₃
90	10	2000	15 »	Glass*
		1950	30 »	Glass*
		1900	30 »	Glass*
		1850	30 »	Glass + Y ₂ O ₃
85	15	2000	30 »	Glass*
		1950	30 »	Glass*
		1900	30 »	Glass + Y ₂ O ₃ · SiO ₂
80	20	2100	15 »	Glass*
		2000	30 »	Glass*
		1950	30 »	Glass + Y ₂ O ₃ · SiO ₂
75	25	2000	30 »	Glass*
		1950	30 »	Glass*
		1900	30 »	Glass + Y ₂ O ₃ · SiO ₂ + + 2Y ₂ O ₃ · 3SiO ₂
70	30	2000	30 »	Glass*
		1950	30 »	Glass*
		1900	30 »	Glass + 2Y ₂ O ₃ · 2SiO ₂
62,5	37,5	1800	30 »	Glass*
		1750	30 »	Glass*
		1700	30 »	Glass + Y ₂ O ₃ · 2SiO ₂
60	40	1850	30 »	Glass*
		1800	30 »	Glass*
		1700	30 »	Glass*
		1650	1 min	Glass + Y ₂ O ₃ · 2SiO ₂ + + SiO ₂ ; Y ₂ O ₃ · SiO ₂ ;
78,9	21,1	1600	10 hrs	Y ₂ O ₃ · SiO ₂ + Y ₂ O ₃ · 2SiO ₂ ;
71,4	28,6	1600	10 »	Y ₂ O ₃ · 2SiO ₂
65,3	34,7	1600	10 »	Y ₂ O ₃ · 2SiO ₂

*In most of the compounds by "glass" is meant a mixture of pure glass and fine crystals, separating out in the annealing process.

TABLE 3. Invariant Points in the Y₂O₃-SiO₂ System

Phase	Process	Composition				Temp. (°C)
		Wt. %		Mole %		
		Y ₂ O ₃	SiO ₂	Y ₂ O ₃	SiO ₂	
Y ₂ O ₃ + Y ₂ O ₃ · SiO ₂ + liquid	Eutectic	87.5	12.5	65.4	34.6	1800
Y ₂ O ₃ · SiO ₂ + liquid	Fusion	78.9	21.1	50	50	1980
Y ₂ O ₃ · SiO ₂ + 2Y ₂ O ₃ · 3SiO ₂ + liquid	Eutectic	75.0	25.0	44.4	55.6	1900
2Y ₂ O ₃ · 3SiO ₂ + liquid	Fusion	71.4	28.6	40	60	1950
2Y ₂ O ₃ · 3SiO ₂ + Y ₂ O ₃ · SiO ₂ + Y ₂ O ₃ · · 2SiO ₂	Reaction in the solid state	71.4	28.6	40	60	1950
Y ₂ O ₃ · 2SiO ₂ + 2Y ₂ O ₃ · 3SiO ₂ + liquid	Incongruent fusion	64.5	35.5	32.5	67.5	1775
Y ₂ O ₃ · 2SiO ₂ + α-cristobalite + liquid	Eutectic	60	40	28.7	71.3	1660
α-cristobalite + liquid ₁ + liquid ₂	Eliquation	57.0	43.0	25.2	74.80	1700
α-cristobalite + liquid ₁ + liquid ₂	Eliquation	5	95	1.4	98.6	1700

Comparison of the results of our investigation and literature data [12] shows that Y₂O₃ has a cubic structure. This structure is preserved also after fusion of Y₂O₃ in an electric arc. The X-ray diffraction curve of this product is shown in Fig. 1B. Round crystals of yttrium oxide, fused in a microfurnace, are shown in the microphotograph (Fig. 3). The general form of the phase diagram obtained by us for the Y₂O₃-SiO₂ system is shown in Fig. 2, a and b. The

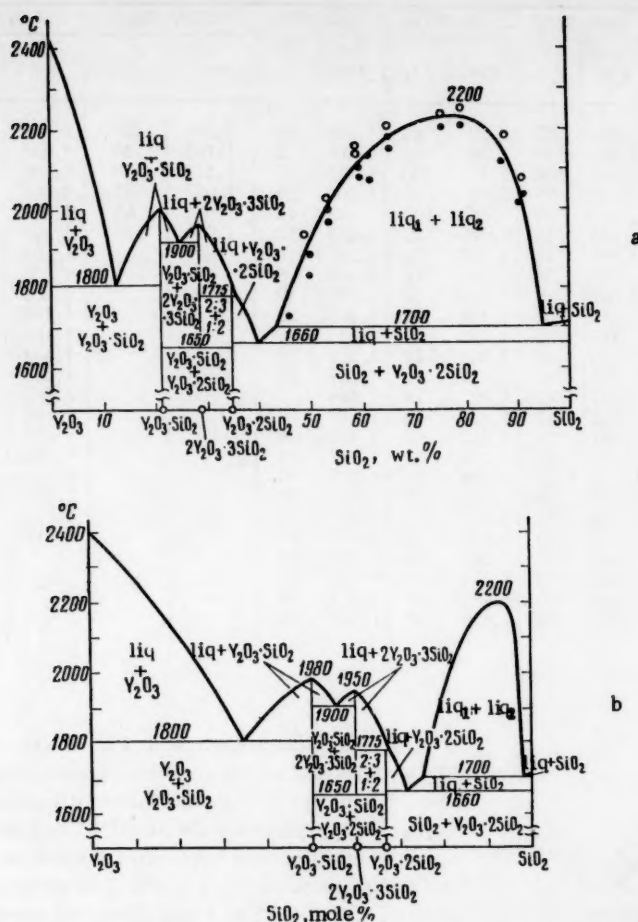


Fig. 2. Phase diagram of the binary system $Y_2O_3-SiO_2$: A) In wt. %; B) in mole %.

results of the firing and annealing experiments are given in Table 2. As is evident from Fig. 2, in the system there is a distinct and considerable separation zone and three chemical compounds: $Y_2O_3 \cdot SiO_2$, $2Y_2O_3 \cdot 3SiO_2$, and $Y_2O_3 \cdot 2SiO_2$.

The temperatures and compositions of the invariant points in the system are given in Table 3.

The 1: 1 Compound, $Y_2O_3 \cdot SiO_2$. melts without decomposition at $1800 \pm 50^\circ$. Crystals of this compound are biaxial, positive, having refractive indices $n_g = 1.825$, $n_p = 1.807$ and average birefringence $n_g - n_p = 0.018$. The X-ray diffraction curve of yttrium silicate is shown in Fig. 1, C and the data calculated from this X-ray diffraction curve is given in Table 4. The formula of the compound $Y_2O_3 \cdot SiO_2$ can be written as Y_2SiO_5 . Here it is possible to substitute three atoms of a bivalent element for the two yttrium atoms ($3Me^{2+} \rightleftharpoons 2Y^{3+}$). This compound can probably be written as yttrium orthosilicate, $Y_2O[SiO_4]$, with regard to its structure.

The 2: 3 Compound, $2Y_2O_3 \cdot 3SiO_2$. melts without decomposition at $1950 \pm 50^\circ$. This yttrium silicate has a stability zone in the temperature range 1950-1650°. At 1650° $2Y_2O_3 \cdot 3SiO_2$ decomposes into a mixture of two compounds, $Y_2O_3 \cdot SiO_2$ and $Y_2O_3 \cdot 2SiO_2$; hence, the indicated process is reversible ($2Y_2O_3 \cdot 3SiO_2 \rightleftharpoons Y_2O_3 \cdot SiO_2 + Y_2O_3 \cdot 2SiO_2$). Experiments showed that the same mixture of 1: 1 and 1: 2 compounds is obtained both by heating the raw oxides in the ratio 2: 3 at 1600° for ten hours and also by exposing the homogeneous product of composition 2: 3 to a temperature of 1600°.

TABLE 4. X-ray Investigation of the Compounds $Y_2O_3 \cdot SiO_2$, $2Y_2O_3 \cdot 3SiO_2$, and $Y_2O_3 \cdot 2SiO_2$

$Y_2O_3 \cdot SiO_2$		$2Y_2O_3 \cdot 3SiO_2$		$Y_2O_3 \cdot 2SiO_2$		$Y_2O_3 \cdot SiO_2$		$2Y_2O_3 \cdot 3SiO_2$		$Y_2O_3 \cdot 2SiO_2$	
d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀
3,83	36	3,60	25	3,59	12	1,509	64	1,194	21	1,447	39
3,48	32	3,42	46	3,39	34	1,462	22	1,183	16	1,438	41
3,30	16	2,907	100	3,12	36	1,445	52	1,173	16	1,386	8
3,09	66	2,852	31	3,07	59	1,399	24	1,097	32	1,305	17
2,98	82	2,629	20	2,863	100	1,368	14	1,084	18	1,284	27
2,867	100	2,435	15	2,605	39	1,351	12	1,061	23	1,258	22
2,765	20	2,279	18	2,453	22	1,329	16			1,252	24
2,641	26	2,208	54	2,381	19	1,314	8			1,235	12
2,521	38	2,087	20	2,275	10	1,291	12			1,209	10
2,393	32	2,035	62	2,188	10	1,266	22			1,188	10
2,292	10	1,948	30	2,103	34	1,215	26			1,164	13
2,246	36	1,903	46	2,065	71	1,202	18			1,153	14
2,165	82	1,866	32	2,030	46	1,187	22			1,143	12
2,016	26	1,827	87	1,925	29	1,168	10			1,105	12
1,971	16	1,812	41	1,842	46	1,136	26			1,094	22
1,939	20	1,591	33	1,812	65	1,123	24			1,076	12
1,878	12	1,575	83	1,740	51	1,087	16			1,062	13
1,837	42	1,543	44	1,700	10	1,079	16			1,049	8
1,810	50	1,533	51	1,675	30	1,063	22			1,036	10
1,737	34	1,458	64	1,655	13	1,049	12			1,024	10
1,719	64	1,357	23	1,614	8	1,042	12			1,017	20
1,671	24	1,305	27	1,567	54	1,032	10				
1,631	15	1,290	32	1,534	37	1,024	18				
1,612	18	1,258	25	1,487	15	1,014	22				
1,562	50	1,233	28	1,459	27	1,007	18				

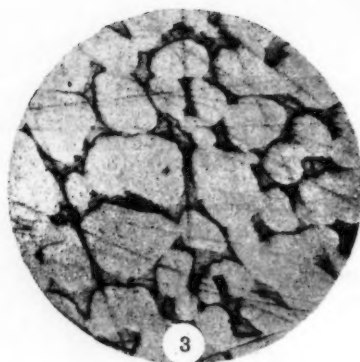


Fig. 3. Round yttrium oxide crystals ($95\% Y_2O_3 + 5\% SiO_2$), 2000° , $\times 240$.

(duration of soaking 30 sec - 1 min) or in a platinum-rhodium furnace at 1600° for about ten hours. Two types of crystals form when the mixture is heated to higher temperatures ($1800-1900^\circ$): primary plate-like crystals of the 2:3 compound, and as a secondary phase, as a result of annealing imperfections, crystals of the 1:2 compound separate out. Hexagonal plates of the $2Y_2O_3 \cdot 3SiO_2$ compound, undergoing resorption, and $Y_2O_3 \cdot 2SiO_2$ crystals are shown in the microphotograph in Fig. 5.

If a similar specimen with 1:2 composition is first of all homogenized (fused in an arc) and is then heated in a microfurnace the formation of hexagonal plates of the 2:3 compound is not observed even at high temperatures ($1800-1900^\circ$). Here, with short duration of soaking (up to 1 min), only crystals of the 1:2 compound separate out. A specimen after arcing also contains only one type of crystal: that of the 1:2 compound. With increase in the

In the microphotographs in Fig. 4, a and b the compound $2Y_2O_3 \cdot 3SiO_2$ and its decomposition products respectively can be seen. By analogy with the lanthanum silicate $2La_2O_3 \cdot 3SiO_4$, $2Y_2O_3 \cdot 3SiO_2$ crystals are characterized by a hexagonal syngony, are optically negative, and have refractive indices $n_0 = 1.780$, $n_e = 1.765$ and birefringence $n_0 - n_e = 0.015$. This compound is yttrium orthosilicate, $Y_4[SiO_4]_3$. The X-ray diffraction curve of $2Y_2O_3 \cdot 3SiO_2$ is shown in Fig. 1,D, and the interplanar distances and line intensities of this X-ray diffraction curve are given in Table 4.

The results of chemical analysis of a specimen of composition 2:3 annealed at 1800° are given in Table 5.

The 1:2 Compound, $Y_2O_3 \cdot 2SiO_2$, melts with decomposition at 1775° into $2Y_2O_3 \cdot 3SiO_2$ and liquid. This was demonstrated by a series of experiments. Thus, it is possible to see only flaky $Y_2O_3 \cdot 2SiO_2$ crystals in the products obtained by heating a 1:2 mixture of the oxides, compressed into tablets, in a microfurnace at $1600-1800^\circ$



Fig. 4. a) Crystals of the 2: 3 compound $Y_4[SiO_4]_3$, 1900° , $\times 240$. b) De-composition of $Y_4[SiO_4]_3$ into $Y_2O[SiO_4]$ and $Y_2[Si_2O_7]$.



Fig. 5. Resorbed $Y_4[SiO_4]_3$ crystals and secondary formation of $Y_2[Si_2O_7]$.

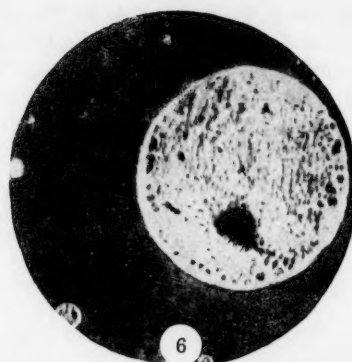


Fig. 6. Region of two immiscible liquids ($20\% Y_2O_3$, $80\% SiO_2$), 2000° , $\times 240$.

TABLE 5. Chemical Analysis Data for a Specimen of $2Y_2O_3 \cdot 3SiO_2$

Composition of the specimen after annealing at 1800° , by analysis (wt. %)	Raw mixture composition, according to the mixture (wt. %)
Y_2O_3 - 71.32	Y_2O_3 - 71.40
SiO_2 - 28.69	SiO_2 - 28.60
Calc. decrease in equiv. wt.	

positive, have mainly skew extinction, refractive indices $n_g = 1.747$, $n_p = 1.737$, birefringence $n_g - n_p = 0.010$, and optic axial angle $2V \approx 60^\circ$. This compound is characterized by a monoclinic syngony and, according to its optical properties, is evidently similar to the mineral thalenite; it is of the pyrosilicate type with composition $Y_2Si_2O_7$. The X-ray diffraction curve of this silicate is shown in Fig. 1, e, and the data calculated from it is given in Table 4.

According to our microscopic investigation, the separation zone is limited. This zone is shown in Fig. 1, a and b as a binodal curve; it is found in equilibrium with the cristobalite zone at 1700° in the concentration region 43.0-95 wt. % (74.8-98.6 mole %) SiO_2 . Separation of one glass in another can be seen in the microphotograph in Fig. 6. In conformity with Levin and Block's work [13] the calculated limiting separation composition equals 28.3 mole %

duration of soaking up to 5-8 min, starting at temperatures of 1800° and higher crystals of the 2: 3 compound appear in such a specimen. In this case it is necessary for the specimen to be enveloped in tungsten before being annealed. Evidently the formation of the 2: 3 compound is slow in a homogenized specimen, and time is necessary for its accomplishment. Besides this, the region in which the primary 2: 3 phase exists is very narrow for specimens with 1: 2 composition, therefore in order to establish its limits it is necessary to carry out the annealing through 30° intervals in the temperature range $1750-1850^\circ$. The investigation showed that $Y_2O_3 \cdot 2SiO_2$ crystals are biaxial,

Y_2O_3 and 71.7 mole % SiO_2 ; the composition which was found experimentally was 25.2 mole % Y_2O_3 and 74.8 mole % SiO_2 .

SUMMARY

1. The phase diagram was constructed and the compositions and temperatures of the invariant points determined for the $Y_2O_3-SiO_2$ system.

2. Three chemical compounds were synthesized: yttrium oxyorthosilicate ($Y_2O_3 \cdot SiO_2$ or $Y_2O[SiO_4]$), yttrium orthosilicate ($2Y_2O_3 \cdot 3SiO_2$ or $Y_4[SiO_4]_3$), and yttrium pyrosilicate ($Y_2O_3 \cdot 2SiO_2$ or $Y_2[Si_2O_7]$).

3. The separation zone was established and some of its characteristics were adduced.

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ADSORPTION OF MIXTURES OF ETHYLENE AND CARBON DIOXIDE ON CARBON BLACK

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From the investigation of the adsorption of mixtures of gases and vapors on the boundaries of the interphase it is possible to draw up the properties of the surface solutions, and to study the non-uniformity of the surface of solid bodies and the properties of the interaction between the adsorbed molecules [1]. However, in the case of the adsorption of binary gaseous mixtures on real porous sorbents the phase diagrams of the surface solutions drawn along the total adsorption isosteres depend, in a complex fashion, on many factors. In the first place they depend on the character of the porosity of the form of the distribution function of the adsorption potentials for sections of the surface, on the magnitude and sign of the forces of the interaction between the adsorbed molecules, on the magnitude of the total adsorption and so on. From this point of view it is obvious that in order to explain the properties of the homogeneous surface solutions it is necessary, as far as possible, to exclude the complications introduced by the porosity of the sorbents and to carry out the investigation of the adsorption of the gas mixtures on an energetically uniform surface. It is possible only under these conditions to compare the surface and volume solutions formed by one and the same pair of substances and on this basis, to assess the possible variations in the properties of the molecules, adsorbed on the surface of a solid body. Commencing from similar conceptions it was decided to investigate the adsorption of binary mixtures of a number of materials on graphitized carbon black possessing a specially uniform surface. In the present paper the results are given which were obtained in the study of adsorption of mixtures of ethylene and carbon dioxide on this adsorbent.

EXPERIMENTAL

The adsorption of individual gases and their mixtures were measured by means of a volumetric method in an apparatus which in its general features was similar to the apparatus used to measure the adsorption of mixtures of CO_2 and C_2H_4 and $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ on active carbon [2]. The amount of each component of the gas mixture was measured volumetrically in a gas burette and then quantitatively transferred to the vessel containing the adsorbent. The vessel was connected to a mercury manometer and electrical gas analyzer based on the measurement of the thermal conductivity of the gas mixture and enabling the composition of the equilibrium gas mixture to be measured. To accelerate the establishment of the adsorption equilibrium an electromagnetic, glass piston pump was used in order to circulate the mixture of gases through the vessel and adsorbent continuously. The whole of the apparatus, excluding the connecting tubes and extensions for the freezing of the gases, was placed at room temperature in a large, wellstirred thermostat, (volume about 100 l) which by means of a toluene thermoregulator and relay was maintained at a constant temperature of 25°C with an accuracy of $\pm 0.002^\circ$. The thermal resistance of the gas analyzer was made of platinum wire, mark "extra", with a length of 104 mm and a diameter of 0.050 mm and the wire was covered with a protective layer of glass by melting a very fine glass capillary slipped over the wire. This glass covered platinum filament proved to be sufficiently stable even with continuous use of the apparatus. The average accuracy in the measurement of the composition of the gas mixture corresponded to $\pm 0.2\%$ of ethylene in the mixture. The gas pressure in the burette and the equilibrium pressure over the adsorbent was measured by two mercury U-shaped manometers (internal diameter of the tubes 14 mm) using a cathetometer for the readings.

Ukhtinskii channel carbon black heated at a temperature of 3000° was used in the experiments. The specific surface of this carbon black, determined by the adsorption of nitrogen vapors was approximately $100 \text{ m}^2/\text{g}$. The slightly moistened carbon black was pressed into small tablets which were then dried at $80-110^\circ$, and 10.15 g of the tablets placed in the adsorption vessel. Prior to carrying out the experiments the carbon black was evacuated at 400° for 6 hr at a vacuum of approximately $1 \times 10^{-6} \text{ mm Hg}$.

The CO_2 was obtained by the thermal decomposition of chemically pure MgCO_3 . The gas evolved was blown through a trap cooled by dry ice and collected in a receiver cooled by liquid nitrogen, and then the solid CO_2 obtained was distilled twice in two receivers placed one after the other, at a pressure of about 10 mm Hg, and the middle fraction was selected. The final purification was carried out by an adsorption method by passing the gas through a tube cooled with dry ice and containing active carbon and silica gel previously heated at 400° in a vacuum.

Ethylene was obtained by the reaction of symmetrical dibromethane with metallic zinc in the presence of copper sulphate. The ethylene was passed through a trap cooled with dry ice and condensed in a vessel cooled with liquid nitrogen and then slowly distilled at a pressure of 5-10 mm Hg in another vessel cooled with liquid nitrogen. After distilling twice at a low pressure the ethylene purified from traces of alcohol is transferred to a cylinder and kept in it under a mercury seal.

A correction due to the fact that ethylene and carbon-dioxide are not ideal gases is made for the equation of state with a second virial coefficient where the values of the virial coefficients were measured with the aid of a burette and manometer in the same apparatus. For mixtures, the virial coefficients were not determined experimentally and their values were found approximately by interpolating between the values of the coefficients for pure gases.

TABLE 1

Adsorption of CO_2 on Carbon Black at Temperatures of 15° and 25° (p, mm of Hg, a, $\mu\text{M/g}$)

Adsorption of C_2H_4 on Carbon Black at Temperatures of 15° and 25° (p, mm of Hg, a, $\mu\text{M/g}$)

p_1	a_1	p_1	a_1	p_2	a_2	p_2	a_2
$t = 15^\circ$				$t = 15^\circ$			
62,5	6,84	331,2	31,7	12,1	5,58	191,2	51,2
111,0	12,0	390,4	37,7	30,5	11,4	232,2	60,8
168,9	16,9	468,4	44,8	46,1	15,3	270,9	70,4
250,5	24,3	538,6	51,5	53,7	18,1	310,9	80,0
				95,7	28,8	349,5	90,2
				151,5	40,8	395,8	100,5
$t = 25^\circ$				$t = 25^\circ$			
24,8	2,83	309,3	22,8	19,0	5,46	127,6	28,0
84,1	7,52	352,0	25,9	24,1	6,63	174,3	36,1
130,9	10,7	443,5	31,8	37,5	9,74	172,6	35,2
138,9	11,0	496,8	35,8	54,2	13,0	221,7	43,8
174,6	13,8	574,5	40,6	71,0	16,8	297,8	56,8
250,7	19,1	581,1	40,7	85,9	19,1		
270,0	19,9	691,9	48,9				

The Adsorption Isotherms of Individual Materials

The measurements of the adsorption isotherms of carbon-dioxide and ethylene on carbon black were carried out at temperatures of 15° and 25° . The experimental results obtained are given in Table 1 and represented graphically in Fig. 1 in which the ordinate represents the values of adsorption in micromoles per gram of adsorbent. For both gases the adsorption isotherms in the initial region are slightly curved but at higher pressures they are practically linear over the whole range studied. The deviation from Henry's law in the initial region should obviously be attributed to a certain non-uniformity of the surface. In the first place it is necessary to note the very small values of adsorption on the active carbon [2]. For the same values of the pressure, the adsorption on the carbon black proves to be 30-60 times less than the adsorption on carbon. Since the specific surface of the carbon black is approximately $100 \text{ m}^2/\text{g}$, but the specific surface of the active carbon AG-2 definitely does not exceed $1000 \text{ m}^2/\text{g}$ then the adsorption on "unit surface" of carbon at the least, exceeds the adsorption on unit surface of the carbon black by 3-6 times.

The differential heats of adsorption q , calculated from the Clapeyron-Clausius equation proved on average to equal 4.8 kcal/M for CO_2 over the range of values of adsorption a_1 from 10 to $35 \mu\text{M/g}$ and 5.6 kcal/M for C_2H_4 in the range of a_2 for 15 to $55 \mu\text{M/g}$. With an increase of the values of adsorption the values of q very slowly diminish. By comparison it has been shown that the differential heat of adsorption of ethylene on carbon AG-2 with small fraction of coverage θ i.e., in the region of specially large non-uniformity, exceeds 10 kcal/M and for a relatively uniform part of the surface of the carbon is close to the value of 5 kcal/M [3]. On this basis it would be expected

that the value would be $q < 5$ kcal/M for a uniform surface of carbon black and consequently the value $q = 5.6$ kcal/M found with a fraction coverage of $\theta < 5\%$ also indicates a certain non-uniformity of the surface.

TABLE 2. Simultaneous Adsorption of CO_2 and C_2H_4 on Carbon Black at 25° (the index 1 is CO_2 , the index 2 is C_2H_4 ; p , mm of Hg, a , $\mu\text{M/g}$)

Series	p_1	p_2	a_1	a_2	p_1	p_2	a_1	a_2
1	—	19,0	—	5,5	125,6	19,5	9,6	5,2
	32,1	18,9	2,4	5,5	199,0	19,4	14,9	5,3
	78,8	18,6	5,5	5,7	258,0	19,4	18,9	5,3
2	—	85,9	—	19,1	131,5	85,8	9,0	19,1
	31,3	85,0	2,0	19,0	198,5	86,2	13,0	19,2
	87,3	85,5	5,4	19,3	259,0	86,4	18,5	19,0
3	—	172,6	—	35,2	143,6	173,0	9,3	35,0
	41,3	172,3	2,3	35,4	187,7	172,5	12,1	35,3
	89,7	172,4	5,6	35,4	239,4	173,2	15,2	35,9

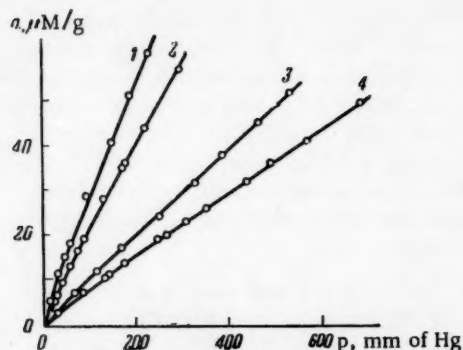


Fig. 1. Adsorption isotherms of ethylene [(1) at 15° ; (2) at 25°] and carbon dioxide [(3) at 15° ; (4) at 25°] on carbon black.

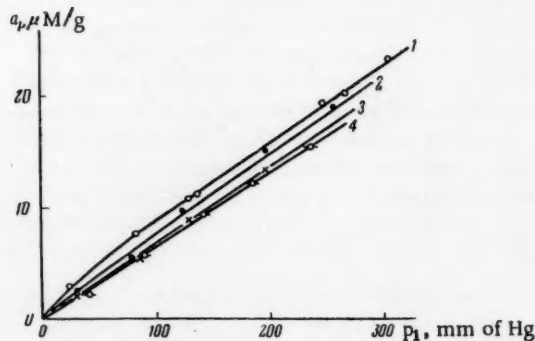


Fig. 2. CO_2 adsorption isotherms with constant values of adsorption of C_2H_4 : 1) $a_2 = 0$; 2) $a_2 = 5.5$; 3) $a_2 = 19$; 4) $a_2 = 35 \mu\text{M/g}$.

Adsorption Isotherms of Gas Mixtures

Three series of tests were carried out on the adsorption of mixtures of ethylene and carbon dioxide at 25° . In each of these series the amount of ethylene in the apparatus remained constant but the amount of carbon dioxide gradually increased. Table 2 reproduces the partial pressures of carbon dioxide p_1 , and ethylene p_2 and the adsorption values of both gases a_1 and a_2 corresponding to these pressures. As can be seen, by considering the figures in Table 2, in each of the three series of experiments the partial pressures p_2 and the adsorption values a_2 of ethylene remained constant within the possible limits of experimental error. Thus with such small coverage of fractions of the surface (not exceeding 6% at the greatest total adsorption of both components) the effect of replacing ethylene by carbon dioxide could hardly be observed. The experimental results obtained for the adsorption of mixtures are given in the form of the CO_2 adsorption isotherm in the presence of a constant amount of adsorbed ethylene, a_2 , equal to 5.5; 19.0 and 35.0 $\mu\text{M/g}$ for all three series of tests. The upper curve, 1 in Fig. 2, represents the separate adsorption isotherm of CO_2 .

Discussion of Experimental Results

As was found earlier [3, 4], with the adsorption of gas mixtures on active carbon and for a series of other systems [5] linear total adsorption isosteres are obtained i.e., the projection of the curves $a_{12} = a_1 + a_2 = \text{const.}$ on the plane p_1, p_2 . The equation for this type of linear isostere takes the following form

$$p_1/p_1^0 + p_2/p_2^0 = 1, \quad (1)$$

where p_1 and p_2 are the partial pressures of the components corresponding to the values of adsorption a_1 and a_2 , p_1^0 and p_2^0 are the equilibrium pressures of the components on the individual adsorption isotherms with $a_1^0 = a_2^0 = a_{12} = a_1 + a_2$

(the index 0 refers to the individual isotherms). The values p_1^0 and p_2^0 may be considered as the "saturated vapor pressure" of the components forming the "surface solution" examined under the condition $a_{12} = \text{const}$, but the values p_1/p_1^0 and p_2/p_2^0 may be considered as the "relative pressures" of the components of the surface solution [1]. Equation (1) is quite accurate for an ideal adsorption system agreeing quite well with a number of known ideal systems (corresponding for example to adsorption on active carbon) and therefore it is natural to expect that it will also apply to the adsorption of mixtures on the much more uniform surface of carbon black. To confirm that Eq. (1) is applicable the isosteres a_{12} were constructed from the interpolated experimental results [3]. But this type of confirmation may be carried out directly from experimental results. In fact, if for each experimental point given by four values of a_1 , a_2 , p_1 and p_2 , we find the values of $a_1 + a_2 = a_{12}$ and from the values $a_1^0 = a_2^0 = a_{12}$ determine p_1^0 and p_2^0 on the individual adsorption isotherms then it is possible to calculate the relative pressures p_1/p_1^0 and p_2/p_2^0 . In the case where Eq. (1) applies, the point with the coordinates p_1/p_1^0 and p_2/p_2^0 must be on a straight line cutting off sections on the coordinate axes equal to unity. The result of this type of confirmation is shown in Fig. 3. The experimental points, referring to the three series of tests for which results are given in Table 2 are given different legends in Fig. 3. The experimental points lie on the inclined line corresponding to Eq. (1), within the limits of experimental error.

In an earlier work [1] it was shown that by studying the adsorption of mixtures of gases it is possible to obtain some idea of the non-uniformity of the adsorbent surface if the "phase diagrams" of the surface solutions constructed along the total adsorption isostere are considered. The surface solution under the condition $a_{12} = \text{const}$, strictly follows Raoult's law for a uniform surface in the case of an ideal adsorption system described by Langmuir's equations

for the adsorption isotherms of a gas mixture. In real adsorption systems a deviation from Raoult's law is observed for surface solutions, negative for the component which is most adsorbed and positive for the component which is least adsorbed. At the same time it was shown that with linear total adsorption isosteres the deviations from Raoult's law must certainly have different signs for both components, while such anomalous behavior of the surface solutions in comparison with the behavior of usual volumetric solutions is obviously determined by the non-uniformity of the adsorbent surface.

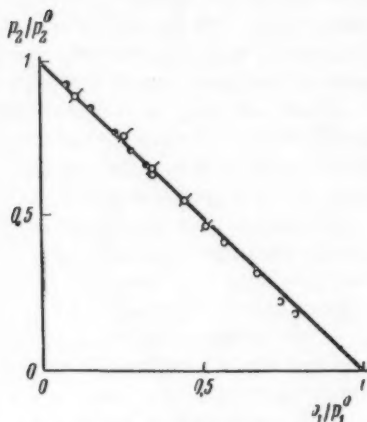


Fig. 3. Linear confirmation of total adsorption isosteres.

In connection with these theories it is of interest to explain the properties of the phase diagrams of the surface solutions for the investigated system. The construction of phase diagrams may be carried out from interpolated results by finding the relation between the partial pressures of both components and the composition of the surface solution N_{O_2} for each isostere. If the deviations from Raoult's law depends very little on the value a_{12} and in the given system, this case is immediately realized as will be shown below, then it is possible to achieve the same end by using the experimental results of Table 2 directly. For this purpose it is sufficient to find the values a_{12} , $N_{O_2} = a_2/a_{12}$, p_1/p_1^0 and p_2/p_2^0 for each experimental point. Then by find-

ing the relation of p_1/p_1^0 and p_2/p_2^0 with N_{O_2} we can reproduce the form of the phase diagram. Figure 4 thus reproduces the phase diagram of the surface conditions for the system under consideration. From the experimental points, designated by different legends corresponding to the three series of tests, it is possible to derive smooth curves for $p_1/p_1^0 = \varphi_1(N_{O_2})$ and $p_2/p_2^0 = \varphi_2(N_{O_2})$ shown by the continuous lines. In the general case the experimental points in Fig. 4 refer to different isosteres $a_{12} = \text{const}$ and therefore they cannot definitely lay on one curve because the position of the curve φ depends on the value of a_{12} . But in the given case in the region of the surface coverage being investigated this relation is so small that it cannot be shown.

The diagonal of the square in Fig. 4 corresponds to an ideal surface solution which follows Raoult's law. The curve φ_1 for CO_2 over the whole range of N_{O_2} lies slightly above the diagonal line given by Raoult's law, but the curve φ_2 lies slightly lower than the corresponding straight line. In other words even for this system the deviation from Raoult's law for the less adsorbing component (CO_2) is positive but for the more adsorbing component (C_2H_4) it is negative. At the same time, the absolute value of the deviations for surface solutions on carbon black is small and the system under investigation is close to the ideal.

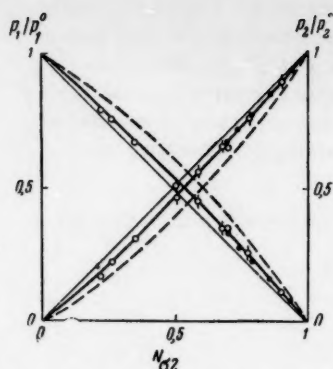


Fig. 4. Phase diagrams of surface solutions on carbon black and on active carbon.

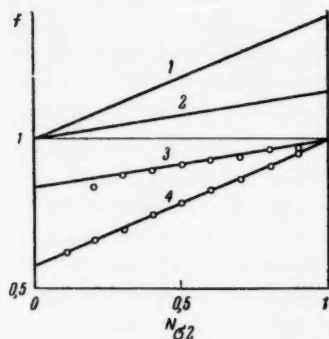


Fig. 5. Relation between the "activity coefficients" and the composition of the surface solution on carbon black (2 and 3, $k = 0.16$) and on carbon (1 and 4), $k = 0.42$.

coefficients f will be presented as complex functions of the non-uniformity of the surface and of the properties of the surface solutions and therefore, for surface phases with large coverages these coefficients cannot obviously be used as quantitative properties of the non-uniformity of the surface.

We shall now explain how the coefficients f_1 and f_2 depend on the composition of the surface solution. Figure 5 gives the relation of f_1 and f_2 with N_{O_2} constructed from the phase diagrams of Fig. 4 for the adsorption of mixtures of $CO_2 + C_2H_4$ on carbon black and on carbon. For both systems the coefficients f_1 and f_2 to a first approximation, are linear functions of N_{O_2} . The coefficient $f_1 = 1$ at the point $N_{O_2} = 0$, and with increase of N_{O_2} increases linearly up to the greatest value at $N_{O_2} = 1$, but the coefficient $f_2 = 1$ at $N_{O_2} = 1$ linearly decreases up to the least value at $N_{O_2} = 0$. On the basis of this empirical relation it is possible to write

$$f_1 = 1 + kN_{O_2} \quad \text{и} \quad f_2 = 1 - kN_{O_2}, \quad (3)$$

where the slope k in both equations has the same value. It is easy to show that under the condition when the total adsorption isotherms are linear the second Eq. (3) is a consequence of the first. In fact, if Eq. (1) applies, then from Eq. (2) it follows that the coefficients f_1 and f_2 are related by the equation

$$f_1N_{O_1} + f_2N_{O_2} = 1. \quad (4)$$

If the value of f_1 from the first equation in (3) is substituted in this equation then the second equation in (3) is obtained.

In Fig. 4 the curves φ_1 and φ_2 are shown by the dotted lines drawn for the system $CO_2 + C_2H_4 +$ carbon AG-2 studied earlier. These curves are very similar in shape to the curves φ for the system under consideration and are different from them only by the larger value of the deviation from Raoult's law.

Thus, in agreement with the results of earlier work [1] the phase diagrams of the surface solutions for the investigated system indicates the existence of a small but distinctly observed non-uniformity of the surface of the carbon black being investigated. This result is found to be in accord with the observed curvature of the separate isotherms in the initial region and the high values of the heat of adsorption of ethylene.

If the "activity coefficients" f_1 and f_2 are introduced for the components of the surface solution, then by analogy with the usual ideal solutions the equation of the curves φ_1 and φ_2 may be described in the following manner:

$$p_1/p_1^0 = f_1N_{O_1}, \quad p_2/p_2^0 = f_2N_{O_2}. \quad (2)$$

In the general form these equations describe the properties of the surface solutions and at the same time represent the most general form of the equations of the adsorption isotherms of the components of the binary mixtures of gases and vapors. As was shown earlier [1], and as can be obviously seen by comparing Eq. (2), with Eq. (1), if the isosteres a_{12} are linear than with f_1 more than 1 f_2 is definitely less than 1 and vice versa.

In all probability this special feature of the coefficients f_1 and f_2 is the consequence of the non-uniformity of the surface and therefore the coefficients f more preferably describe this non-uniformity than the properties of the uniformity of the surface phase. In any case, this result appears to us as very probable for the evacuated surface solutions with which we are dealing in the case under consideration, because for an ideally uniform surface the individual adsorption isotherms will be described in the initial region by the equations of Henry or Langmuir and therefore the evacuated surface two component phase must follow the law of Raoult. However, in the general case the coef-

The numerical values of the slopes of the straight lines in Fig. 5 for carbon black are $k = 0.16$ and for active carbon $k = 0.42$. We note that in the case of adsorption of mixtures of ethylene and propylene on the same carbon the relation between the coefficients f_1 and f_2 and $N\sigma_2$ is also linear, while the slope k at 25° is equal to 0.40 i.e., it is fairly close to the value of k for mixtures of $\text{CO}_2 + \text{C}_2\text{H}_4$. On this basis it is possible to consider that the value of k , found to be equal to 0.16 for carbon black, is a type of numerical property of the non-uniformity of its surface. This property will probably also retain its value for mixtures of other materials. However, this theory naturally requires further experimental confirmation.

If the values of f_1 and f_2 from Eq. (3) are substituted in Eq. (2) then the following expression for the partial pressures of the components along the total adsorption isostere is

$$\begin{aligned} p_1 &= (1 + kN_{\sigma_2}) N_{\sigma_1} p_1^0, \\ p_2 &= (1 - kN_{\sigma_1}) N_{\sigma_2} p_2^0 \end{aligned} \quad (5)$$

or in a somewhat more symmetrical form:

$$\begin{aligned} p_1 &= (N_{\sigma_1} + kN_{\sigma_1}N_{\sigma_2}) p_1^0 = (N_{\sigma_1} + \delta) p_1^0, \\ p_2 &= (N_{\sigma_2} - kN_{\sigma_1}N_{\sigma_2}) p_2^0 = (N_{\sigma_2} - \delta) p_2^0, \end{aligned} \quad (6)$$

where $\delta = kN_{\sigma_1} N_{\sigma_2}$, obviously represents the value of the deviation from Raoult's law. These deviations for an ideal system are equal to zero and consequently $k = 0$. For real systems the deviations are proportional to the coefficient k which therefore may be considered as a property of the non-uniformity of the surface with any case with small coverage fractions when the interaction between the adsorbed molecules still does not develop.

The expression (5) represents a semi-empirical equation of the adsorption isotherms for a binary mixture of gases. If the coefficient k is known then for each given pair of values of a_1 and a_2 it is possible to calculate the corresponding values p_1 and p_2 from these two equations because p_1^0 and p_2^0 may easily be found for the individual adsorption isotherms of the components. To confirm the applicability of Eqs. (5) to the experimental results in Table 2, we calculated the partial pressures p_1 and p_2 of both gases with constant values of the adsorption of ethylene equal to 5.5, 19 and 35 $\mu\text{M/g}$ for a series of values of a_1 from 0 to 20 at intervals of 2 $\mu\text{M/g}$. In Fig. 2 the continuous lines represent the adsorption isotherms of CO_2 calculated in this way. As can be seen from Fig. 2 the experimental points designated by a different legend for each series lie fairly well on the calculated curves if the comparatively large scatter of the experimental points are considered as brought about by the small values of adsorption on carbon black. In Table 3 as an example, we have also derived the partial pressure p_2 of ethylene calculated from the second of the equations in (5) for series 2 with $a_2 = 19 \mu\text{M/g}$ with the values of a_1 given in Table 2 for this series. Comparison of the calculated values p_2 with those directly measured shows that the second equation in (5) agrees quite well with experiment and gives a constant value of p_2 along the curve $a_2 = 19$ in Fig. 2. Thus with the given individual adsorption isotherms of the empirical value $k = 0.16$ the

TABLE 3. Comparison Between the Measured and Calculated Values of p_2

p_2 measured	p_2 calculated
86,0	84,5
85,5	85,0
85,8	84,5
86,2	85,4
86,4	86,8
Average 86,0 \pm 0,2	85,2 \pm 0,7

equations in (5) describe all the experimental results for the adsorption of mixtures of $\text{CO}_2 + \text{C}_2\text{H}_4$ on carbon black quite satisfactorily. This equation may be just as well applied for the case of adsorption of mixtures of $\text{CO}_2 + \text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ on carbon. To illustrate this we have derived Fig. 6 in which curves 1, 2, and 3 represent the adsorption isotherms of ethylene calculated from the equations in (5) with $k = 0.40$ for the three series of experiments on the adsorption of mixtures of ethylene and propylene on active carbon, and the circles represent the experimental points. The top curve in Fig. 6 represents the separate adsorption isotherm of ethylene. An approximately similar agreement between the calculated and measured values of the partial pressures of CO_2 was found for the system $\text{CO}_2 - \text{C}_2\text{H}_4 - \text{carbon}$.

In conclusion let us refer to the problem of the adsorption selectivity coefficient α_2 . If the values p_1 and p_2 from the equations in (2) are substituted in the expression for this coefficient, then we obtain

$$\alpha_2 = \frac{a_2}{a_1} \cdot \frac{p_1}{p_2} = \frac{p_1^0}{p_2^0} \cdot \frac{f_1}{f_2} = \alpha_2^{\text{id}} \cdot \frac{f_1}{f_2}, \quad (7)$$

where the selectivity coefficient for an ideal system [5]

$$\alpha_2^{\text{id}} = p_1^0/p_2^0. \quad (8)$$

Equation (7) indicates that the selectivity coefficient α_2 for a non-uniform surface is always more than the selectivity coefficient on a uniform surface, α_2^{sel} , because $f_1 > f_2$. Along the total adsorption isostere, α_2 varies in proportion to the value of the ratio f_1/f_2 .

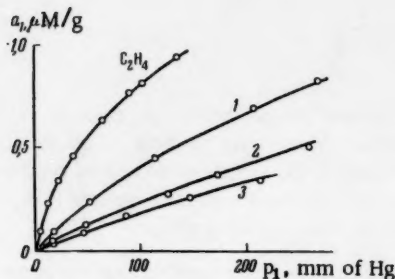


Fig. 6. Confirmation of the applicability of Eq. (5) to the adsorption of mixtures of ethylene and propylene on active carbon at 25°.

deviations indicated that there was a small non-uniformity of the surface of the carbon black.

3. In the system studied the "activity coefficients" of the surface solutions are linear functions of the composition of the adsorption phase with same values of the slope. For carbon black this coefficient (the value of the slope) is equal to 0.16 and in the case of evacuated surface phases it is possible to consider this coefficient as a numerical property of the non-uniformity of the surface. An analogous relation between the activity coefficients and the composition is found for the surface solutions in the adsorption of mixtures of $\text{CO}_2 + \text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ on active carbon.

4. The semi-empirical equations found for the adsorption isotherms of the components of binary gas mixtures permit the experimental results obtained for the adsorption of gas mixtures on carbon black and active carbon to be obtained with sufficient accuracy from the individual adsorption isotherms and the coefficient of non-uniformity of the surface.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

THE TEXTURE AND ADSORPTIVE PROPERTIES OF CHROMIC OXIDE AND HYDROXIDE

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Among the oxidic catalysts for hydrogenation, oxidation, dehydration and isotopic exchange, chromic oxide is of highest importance. In wideness of practical application chromic oxide, perhaps, is only outdone by the alumina catalyst: it is a component of several important catalysts for polymerization [1, 2], aromatization of oil products [3, 4] and so on. However, even chromic oxide itself is a very active catalyst for many organic reactions [5-8], on which, for example, in the $\text{RH} + \text{D}_2$ reaction exchange takes place at and below room temperature [9, 10].

In the scientific literature much attention is paid to studying the catalytic, magnetic and adsorptive properties of chromic oxide, its structure and method of preparation, but, in spite of that, until now the origin of its activity and the mechanism of many processes remain incompletely clear. It seemed to us that an investigation of the surface properties, chemical structure of the surface layers in combination with that of the texture, which has a great influence on the kinetics of a catalytic reaction, would contribute to a further clarification of the activating action of chromic oxide. In many cases it is expedient to investigate the surface properties and the porous structure of chromic oxide formed at or above room temperature, since in many reactions already at these temperatures such a chromic oxide shows an appreciable activity. In the present study we have studied the surface properties and the texture of chromic oxide by means of the adsorption method while using adsorbates with various structures.

Experimental Part

In the preparation we have started from the chromic hydroxide $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ obtained by mixing 10 weight% solutions of $\text{Cr}(\text{NO}_3)_3$ and NH_4OH at a temperature of 40° . The final value of the pH in the solution over the precipitate was 8.8. The precipitates were washed out at room temperature in order to remove the NO_3^- ions and were dried during four hours at a temperature of 120° . This adsorbent had an intensive gray-green color; separate portions of it were pumped out to a high vacuum of $3 \cdot 10^{-5}$ mm Hg: during 25 hr at room temperature (sample 1A), then during 20 hr at $120 \pm 5^\circ$ (sample 1B) and then at 280° during 26 hr (sample 1C). Besides, sample 1D was prepared by evacuating sample 1B at 450° during 20 hr in the adsorption apparatus, after it had been used in a series of adsorption experiments.

As a result of the above described differences in the thermal treatment, the samples had a different water content. The analysis of the total water content (adsorbed plus structural water) was done by heating portions of the samples evacuated under the conditions indicated in a platinum crucible at 1200° to constant weight. In this, the total loss in sample weight was ascribed to removal of water. Besides, the amounts of moisture removed during the evacuation were determined. The results of these determinations are given in Table 1.

The adsorption measurements were done in a sealed all-glass vacuum apparatus of the volumetric type. The apparatus used, which has been described previously in detail [11-12], is a combination of the volumetric method and a vacuum microburet. The pressures were measured by means of an U-shaped manometer and the positions of the liquid meniscus in the microburet were read with an accuracy of ± 0.01 mm by means of a KM-6 cathetometer. The accuracy of the adsorption measurements was $\pm 1 \mu\text{mole}$ (at $p/p_s = 0.1$) in the volumetric method and $\pm 6 \mu\text{mole}$, when the microburet was used.

Commercial nitrogen and argon were purified by the method indicated in Brauer's monograph [13]. Benzene and n-hexane were distilled over metallic sodium. Moreover, the benzene was three times recrystallized by freezing.

Both liquid adsorbates were outgassed in the vacuum apparatus. Methyl alcohol was distilled over metallic calcium and in a similar way outgassed in the vacuum apparatus until the air had been expelled.

The data on the water content, as were obtained by pumping off and heating the chromic hydroxide, are given in Table 1.

TABLE 1. Water Content and Weight Loss During Pumping Off

Sample	Evacuation temperature, °C	Weight loss during pumping off, %	H ₂ O content, %	Composition
1A	20	8,9	35,8	Cr(OH) ₃ ·0,85 H ₂ O
1B	120	20,1	24,5	Cr(OH) ₃ ·0,1 H ₂ O
1C	280	37,5	8,1	Cr ₂ O ₃ ·0,72 H ₂ O
1D	420	41,1	3,0	Cr ₂ O ₃ ·0,25 H ₂ O

From Table 1 it is evident that the first two samples, essentially, are Cr(OH)₃ hydroxides with different degrees of hydration. An analysis of the x-ray diffraction patterns obtained in our laboratory by V. M. Akimov and L. D. Kretalova has indicated that these samples are x-ray amorphous.

The study of the adsorptive properties led to the following results:

Cr₂O₃ Sample 1A. The Cr₂O₃ sample 1A was a typical Cr(OH)₃ hydroxide with an excess of water, which, obviously, was bonded rather strongly to the hydroxide, since it was not completely expelled by pumping off during more than 25 hr at room temperature in a high vacuum. However, it seems to us that the incompleteness of the water expulsion from the hydroxide originates from the slowness of the diffusion of its molecules from the bulk to the surface of the hydroxide through the blocking layer of the stoichiometric chromic hydroxide formed.

On the Cr₂O₃ sample 1A we have carried out a cycle of adsorption measurements in the following sequence: nitrogen and argon at the temperature of liquid nitrogen, n-C₆H₁₄, C₆H₆ and CH₃OH to 20°. In order to get reproducible results we did a series of measurements with each adsorbate comprising adsorption, desorption, evacuation, another adsorption and desorption. The results of the adsorption measurements are presented in the form of the vapor sorption isotherms shown in the Figs. 1 and 2. It should be noted that the repeated adsorption of nitrogen, n-hexane and benzene does not coincide with adsorption for the first time, although the desorption branch in the region of low pressures completely matches the adsorption branch. An additional pumping off during 20 hr resulted in a raised nitrogen sorption, because by this treatment the sample 1A had been further dehydrated (Fig. 3). The adsorption isotherms of N₂, Ar and CH₃OH were determined in the range of small p/p_s up to 0.3-0.5. The adsorption isotherms of C₆H₆ and C₆H₁₄ were measured in a broad range of relative pressures up to 0.95. The shape of the C₆H₆ and C₆H₁₄ isotherms is that characteristic for coarse powderous materials with a great macropore volume. The small magnitude of the adsorption points also in this direction. On sample 1A the adsorption of methanol is irreversible (Fig. 2). The amount of chemisorbed CH₃OH was 0.2 mmole, which corresponds to about 50% surface coverage.

By applying the BET equation to the adsorption data we were able to estimate the specific surface area, the amounts of the various adsorbates giving a complete monolayer and the areas occupied by the adsorbed molecules in a complete monolayer. The results of these calculations are assembled in Table 2.

Sample 1B. The adsorption isotherm of nitrogen on sample 1B at -195° is shown in Fig. 3. As is evident from this figure, the sorption of nitrogen on sample 1B is practically the same as that on sample 1A evacuated after the first adsorption. Therefore, on the sample 1B the behavior of the other adsorbates was not studied. The data on the water content of sample 1B indicate that it too is a chromic hydroxide, consequently, in adsorptive properties it is analogous to sample 1A.

Sample 1D. This sample contained the smallest amount of H₂O and, essentially, was already a partially hydrated chromic oxide in which the hydroxyl groups were distributed statistically over the entire volume of the oxide.

The isotherms for this sample are shown in Fig. 1 in order to compare them with those for sample 1A. From Fig. 1 it is evident that a continuation of the thermal outgassing gives rise to increased adsorption, but that meanwhile hysteresis, which is characteristic for catalysts with micropores or intermediary pores, does not appear. The

TABLE 2. Values of the Specific Surface Area, Monolayer Capacity and Molecular Area

Sample	Nitrogen		Argon		n-Hexane		Benzene			Methanol		
	s m ² /g $\omega_0=16.2$	a_m mmole/g	s m ² /g $\omega_0=15.7$	a_m mmole/g	s m ² /g $\omega_0=15.7$	ω_0 Å ²	C_{BET}	a_m mmole/g	ω_0 Å ²	C_{BET}	a_m mmole/g	ω_0 Å ²
1A	53	0,541	0,536	50	0,226	39	54	(0,211)	(42)	(42)	0,319	23
1B	55	0,56 ₁	—	—	0,207	(42)	(15)	—	—	—	—	—
1D*	159	1,63 ₄	1,53 ₈	136	0,448	59	73	0,593	44	55	—	—

*The values of s and a_m were calculated per gram of the original hydroxide 1B.

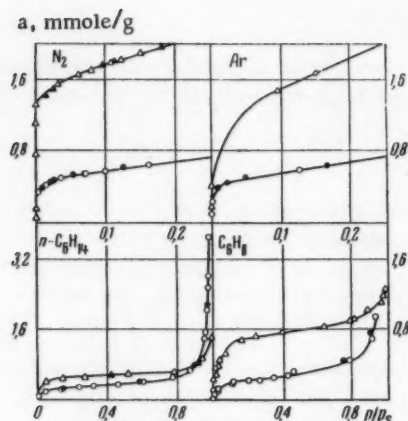


Fig. 1. Adsorption isotherms of nitrogen and argon at -195° and those of $n\text{-C}_6\text{H}_{14}$ and C_6H_6 at 20° on the samples 1A(O) and 1D(Δ); filled points denote desorption.

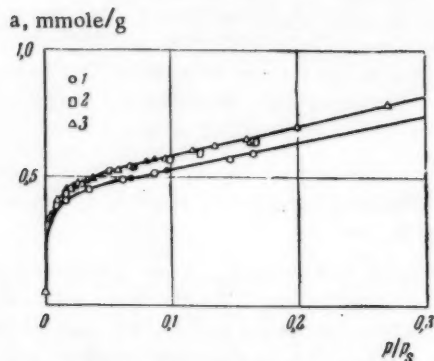


Fig. 3. Adsorption isotherm of nitrogen vapor at -195° on sample 1A: 1) first series of measurements; 2) second series of measurements done after an additional outgassing; 3) 1B (filled points denote desorption).

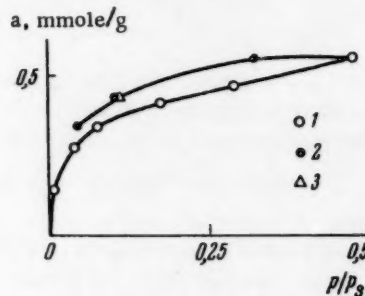


Fig. 2. Sorption isotherm of CH_3OH vapor at 20° on sample 1A: 1) first adsorption; 2) desorption; 3) second adsorption.

increase in adsorptive capacity originates from the formation of new dividing surfaces during the spontaneous break down of the substance aggregates; this break down is caused by the topochemical phase change and finds its expression in the theory of topochemical reactions developed by Tompkins and Prout [14]. The raised dispersity of secondary formations should be accompanied by an increased surface area. A similar phenomenon has been noticed by de Boer, Steggerda and Zwietering [15] in the decomposition of aluminum hydroxide.

The surface area of sample 1D was calculated by means of the BET method and the data obtained are given in Table 2.

It should be noticed that in the case of benzene on sample 1A the BET equation is not satisfied so that the values given in Table 2 and enclosed in parentheses are provisory and unreliable, although they appear to be plausible. For methanol in Table 2 we have used only adsorption data; a calculation from the desorption branch of the isotherm gives $\omega_0 = 21 \text{ Å}^2$, a value, which is also often obtained for oxidic catalysts [16]. For $n\text{-C}_6\text{H}_{14}$ in Table 2 two series of values are given, namely those for the first and the second adsorption.

Discussion of the Experimental Results

The adsorption data show that, when the temperature of outgassing the chromic hydroxide in vacuum is raised, simultaneously with the expulsion of the water in excess there take place changes in the texture accompanied by an increase in surface area and dispersity of the agglomerates constituting the skeleton of the catalyst. If it is assumed that these agglomerates have a spherical shape, one may calculate the size of these spherulites from the surface area by taking for the density of $\text{Cr}(\text{OH})_3$ $\rho = 2.7 \text{ g/cm}^3$ and for Cr_2O_3 $\rho = 5.2 \text{ g/cm}^3$. The calculation gives $D = 400 \text{ \AA}$ and $D = 70 \text{ \AA}$, respectively, where D is the diameter of such an agglomerate.

The amounts adsorbed, when calculated per unit surface area, give a numerical representation of the change in surface properties. In Fig. 4 the absolute adsorption isotherms of N_2 , Ar, $n\text{-C}_6\text{H}_{14}$ and C_6H_6 for the samples 1A and 1D are shown. These isotherms were obtained from the experimental isotherms by dividing the amount adsorbed by the specific surface area found from nitrogen adsorption. The argon isotherms are exceptions, since for them we took the specific area derived from argon adsorption. In other words, the upper part of Fig. 4 illustrates the reduction of isotherm to its absolute value. These absolute isotherms prove that, with respect to argon, there is found no noticeable change in the surface properties (the amounts of Ar adsorbed per unit area for 1A and 1D lie on a single smooth curve, the values of the constant, C_{BET} , are 124 and 136, respectively), whereas the hydration degree of the surface layers has an influence on the adsorption of nitrogen (in the initial region of the isotherm the amounts of N_2 adsorbed on sample 1D are greater than those on sample 1A and C_{BET} has a higher value: 306, instead of 190). Benzene behaves itself analogously to nitrogen; however, some uncertainty in the calculated values given for sample 1A in Table 2, which, obviously, results from the effect of the high water content in the chromium hydroxide leading to a strong moistening of the benzene, does not allow one to use these values with confidence in the comparison.

Hexane behaves itself very strangely: the effective adsorption per 1 m^2 is higher for the original sample 1A than for 1D. This is quite evident from the value of ω_0 for C_6H_{14} . The value $\omega_0 = 39 \text{ \AA}^2$ is somewhat low for non-porous and wide-porous adsorbents. Obviously, the behavior of C_6H_{14} may have two reasons. Firstly, the raised adsorption may result from a strong physical interaction between the C_6H_{14} molecules and the uncovered surface of the chromic hydroxide and from a certain chemical affinity of the hydrocarbon molecule to chromium ions; secondly, the specific area of $\text{Cr}(\text{OH})_3$ may be lowered with respect to the value determined from nitrogen adsorption. The second reason seems to us more probable, since during the protracted outgassing in the presence of small fractions of adsorbed molecules there takes place further dehydration of the sample, which is accompanied by a rise in the surface area. The comparatively high values of C_{BET} and the fact that the first and the repeated adsorption do not coincide, while the former is greater than the latter, are arguments to the advantage of the first reason.

The paper by Rode and Agronomov [17], which has appeared recently and is devoted to an adsorption study on Cr_2O_3 , raises objection, since it explains the color of Cr_2O_3 by the character of the porosity. It seems to us that the reason for the various colorations of Cr_2O_3 lies in different valence states of chromium or in an excess of oxygen in the Cr_2O_3 lattice [18]. These causes may also be responsible for the raised adsorption of n -hexane vapor.

SUMMARY

1. Prolonged outgassing of chromic hydroxide at room temperature results in the formation of unstable phases, which at the additional evacuation between successive adsorption measurements may lead to a further change. Outgassing under heating is accompanied, besides by dehydration, by a break down of the chromic hydroxide particles: the surface area is increased by three times.
2. The samples obtained show specific surface properties: methanol is chemisorbed strongly on the chromium hydroxide surface, n -hexane on chromium hydroxide is characterized by an adsorbability raised in comparison with that of benzene.

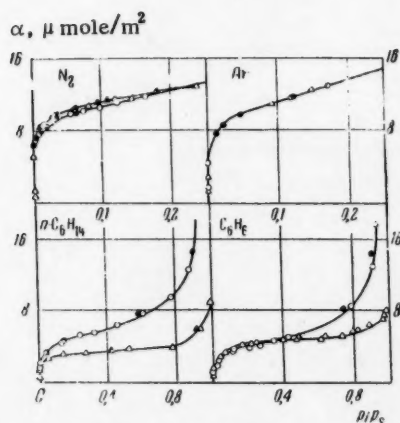


Fig. 4. Absolute adsorption isotherms of N_2 , Ar, C_6H_{14} and C_6H_6 for the samples 1A(O) and 1D(Δ).

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ON THE INFLUENCE OF THE RADIOACTIVE RADIATION OF A SOLID BODY ON ITS CATALYTIC PROPERTIES

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In recent years irradiation with gamma rays or with neutrons has been rather widely used to affect the processes of heterogeneous catalysis. However, there is a lack of data in the literature on the influence of radioactive radiation from the solid bodies themselves on their catalytic properties. In one of our investigations [1] the catalyst itself was the source of ionizing radiation for a reaction of heterogeneous gas catalysis. It was shown that by the introduction of S^{35} one could observe an increase in the catalytic activity of magnesium sulfate and sodium sulfate on the dehydration of cyclohexanol. It appeared interesting to understand how the catalytic activity changes as a function of the decomposition of the radioactive isotope, to see if the beta radiation of the isotope influences the reaction under study, and to investigate how external irradiation of the catalyst with a stream of fast electrons affects it.

Experimental Part

Catalysts containing radioactive sulfur were prepared from inactive recrystallized magnesium sulfate (C.P.) by the addition of radioactive (with sulfur) sodium sulfate simultaneously with stable sodium sulfate (C.P.) as the carrier. The ratio of S^{35} to ordinary sulfur was 1.8×10^{-10} . An aliquot of the magnesium sulfate of approximately 0.7 g was dissolved in water, and to this was introduced a definite quantity of a solution of active sodium sulfate; an ionic exchange occurred. The solution was evaporated, the salt was gradually heated to 400° , and was maintained at this temperature for 1.5 hours. To obtain comparable results, radioactive and non-radioactive catalysts were prepared with identical contents of sodium sulfate; in the one case stable (C.p.), in the other — radioactive.

The catalyst which contained the radioactive isotope of calcium was prepared by the addition of solid magnesium sulfate to a saturated solution of calcium chloride at the boiling point with subsequent evaporation to dryness; the residue was maintained at a temperature of 400° for 1.5 hours. The non-radioactive catalyst was prepared in exactly the same way.

The kinetic experiments were carried out in a catalytic quartz apparatus of the flow-through type furnished with an automatic supply of substance and with an inserted reactor [2]. Thanks to the use of a derivative automatic temperature regulator [3] there was attained a sensitivity of maintenance of temperature in the tube furnace of $\pm 0.25^\circ$. In the reactor were placed granules of the catalyst with a diameter of from 1 to 2 mm. The cyclohexanol starting material had a b.p. of 70° (20 mm; n_D^{30} 1.4625; d_4^{30} 0.9445). The experiments were carried out over the temperature interval $355-420^\circ$ for an input of the cyclohexanol of volume rate 0.4 min^{-1} . The weight of the catalyst was known and was usually equal to 0.25 g. Every experiment lasted 30 min. The degree of conversion of the cyclohexanol was determined by the method of bromometric titration of an aliquot of the catalyzate obtained during the second 15 min. after the beginning of the experiment. The catalytic activity was characterized by the degree of dehydration of the cyclohexanol attributed to a unit weight of the catalyst.

It turned out that the addition of ordinary sodium sulfate to magnesium sulfate led to a noticeable decrease of the catalytic activity of the latter. The effect of the addition of calcium chloride was analogous (Fig. 1). Therefore for the elucidation of the influence of the radioactive isotopes, the kinetic experiments were carried out for pairs of catalysts: 1) radioactive with a known content of the radioactive isotope, and the other catalyst of the pair —

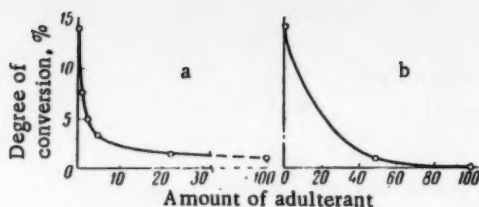


Fig. 1. The dependence of the catalytic activity of MgSO_4 on adulteration.

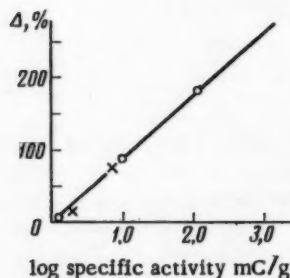


Fig. 3. The dependence of the increase of the degree of conversion of cyclohexanol on the logarithm of the specific activity of the catalyst (410°). The small circles designate Δ for catalysts of respective specific activities - 1.26 (6^*), 9.2 (5^*) and 105.2 (4^*) mC/g; the small crosses designate Δ for the catalyst 4^* when its activity was investigated after $\tau_1 = 314$ days and $\tau_2 = 188$ days more.

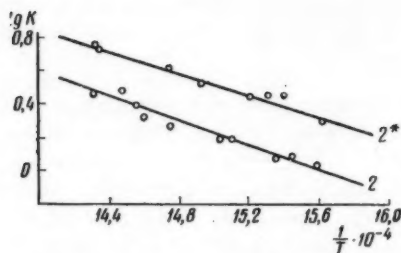


Fig. 5. The dependence of the logarithm of the rate constant on the inverse temperature for the dehydration of cyclohexanol. 2) $\text{MgSO}_4 + 50.86\% \text{ CaCl}_2$ (non-radioactive); 2^*) $\text{MgSO}_4 + 50.86\% \text{ CaCl}_2$ (radioactive).

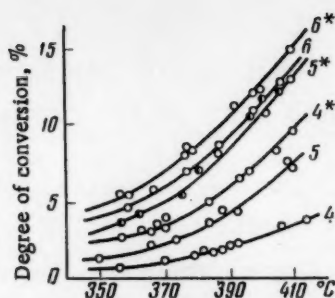


Fig. 2. The influence of the radio-activity of the catalyst on its catalytic activity.

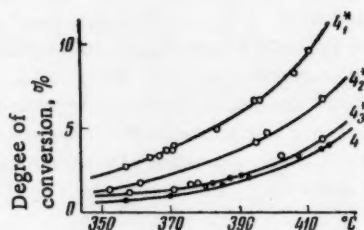


Fig. 4. The influence of the radio-activity of the catalyst 4_{1-3}^* on its catalytic activity.

non-radioactive; however the ratio of sodium sulfate to magnesium sulfate or of calcium chloride to magnesium sulfate in each pair was the same. The same number was given to the catalysts of such pairs. The number of the radioactive catalyst was marked with an asterisk as is shown in Fig. 2.

If the degree of conversion of the cyclohexanol, under certain conditions on the radioactive catalyst is designated by a^* and on the non-radioactive catalyst by a , then the increase in the degree of conversion on the radioactive catalyst is

$$\Delta = \frac{100(a^* - a)}{a} \%$$

The dependence of Δ on the absolute specific activity of the catalyst for catalysts containing different quantities of radioactive S^{35} is shown in Fig. 3. The increase of the degree of conversion of the cyclohexanol on the radioactive catalyst increases together with the growth of its radioactivity.

The radioactive catalyst 4_1^* which contains 78.13% MgSO_4 and 21.87% Na_2SO_4 initially had a specific activity

of 105.2 mC/g and was characterized by a value of Δ equal to 171%. After 314 days the specific activity of this catalyst had fallen to 8.5 mC/g, and the increase of the degree of conversion of the cyclohexanol on it was only 76% (this catalyst is designated below as catalyst 4₂*). After still another 188 days the specific activity of the catalyst had fallen to 1.9 mC/g and Δ had decreased to 12%. This catalyst was designated 4₃* (Fig. 4).

The results obtained are very interesting. In the first place they show that the increase of catalytic activity is actually connected with the radioactivity of the catalytic sample since on decrease of its radioactivity (with otherwise equal conditions) the catalytic activity of the catalyst proportionately falls; secondly since the effect does not accumulate in proportion to the decomposition of the radioactive isotope, it is not due to the products formed from the decomposition of the radioactive isotope S³⁵.

TABLE 1. The Apparent Activation Energy of the Dehydration Reaction of Cyclohexanol

Catalyst	Catalyst number	Catalyst characteristics		Number of experiments	Apparent activation energy, kcal/M
		wt. % content of MgSO ₄	absolute activity, mC/M		
MgSO ₄ with various amounts of Na ₂ SO ₄	1	100,00	0,0	6	15,2
	2	0,00	0,0	11	23,8
	3	97,93	0,0	11	20,1
	4	78,13	0,0	11	20,8
	4*	78,13	105,2	9	19,2
	5	95,94	0,0	8	21,4
	5*	95,94	9,2	9	19,2
	6	99,48	0,0	9	16,4
	6*	99,48	1,26	9	15,5
The mixture MgSO ₄ (78.13%) and Na ₂ SO ₄ (21.87%)	4 ₁ *	78,13	105,2	9	19,2
	4 ₂ *	78,13	8,5	5	21,0
	4 ₃ *	78,13	1,9	7	21,0
MgSO ₄ with added CaCl ₂	2	49,14	0,0	10	10,0
	2*	49,14	10,13	8	14,2

TABLE 2. The Dependence of the Dose Rate on the Current to the Monitor Chamber

The current at the monitor chamber in microamps	The dose rate in ev/ml·sec
600	0,8 · 10 ¹⁷
800	1,1 · 10 ¹⁷
900	1,3 · 10 ¹⁷
970	1,4 · 10 ¹⁷

It is interesting to notice that calcium chloride is not a catalyst for the dehydration reaction; it gives the same effect as quartz, which was inserted into the reactor in the form of small grains of diameters from 1 to 2 mm (as in all other experiments with catalysts). Calcium chloride under the same conditions appears to be an indifferent additive to the magnesium sulfate; in the case of the non-radioactive catalyst it led to a strong decrease of the degree of conversion of the cyclohexanol. Nevertheless, for the radioactive catalyst of this pair there was again observed an increase in the degree of conversion of the cyclohexanol which followed the same law as in the case of the introduction of S³⁵ (Fig. 5).

In all the kinetic experiments the degree of conversion of the cyclohexanol was small, and we equated it to the reaction rate constant with little error [4]. Further, the apparent energy of activation of the reaction was graphically determined according to the Arrhenius equation. From Table I it is obvious that the apparent activation energy increases with the increase of the amount of sodium sulfate added to the magnesium sulfate. The introduction of the radioactive isotopes S³⁵ and Ca⁴⁵ somewhat decreases the apparent activation energy.

To examine the proposition that the continuous bombardment with beta particles might influence the processes being effected at the boundary of the solid substance and the gas, experiments were carried out in which the catalyst was irradiated during the time of the reaction by a beam of 800 kev electrons; these were obtained from an electron accelerator which consisted of a vertically sectioned tube for direct acceleration and a cascade voltage multiplier. In this way the energy of the external ionizing radiation was known to exceed by approximately 4.8 times the energy

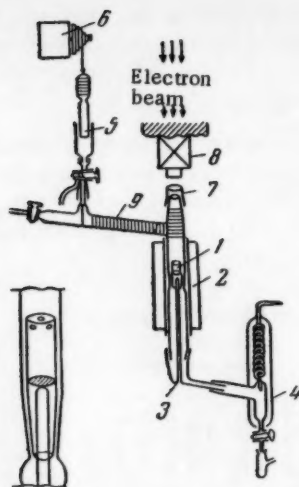


Fig. 6. Apparatus for the study of the action of ionizing radiation on the catalyst during the reaction: 1) Reactor with catalyst (an enlarged view of the reactor is depicted at the left); 2) furnace; 3) quartz sleeve for the thermocouple; 4) catalyze receiver; 5) syringe for the reactant; 6) pulley for the automatic supply; 7) molybdenum glass window (100μ thickness); 8) ionization chamber of the electron accelerator; 9) evaporator.

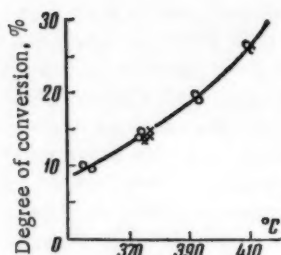


Fig. 8. The dependence of the degree of conversion of cyclohexanol on the temperature over C.P. MgSO_4 . The small circles designate experiments without irradiation; the small crosses designate experiments in which the catalyst was irradiated with 800-kev electrons during the reaction.

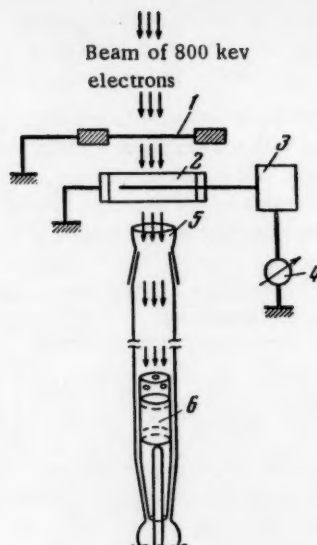


Fig. 7. Design of the experiments for the dosimetry of the electron beam: 1) beryllium exit window; 2) ionization chamber monitor; 3) stabilized source; 4) microammeter; 5) window of the catalytic apparatus; 6) vessel with FeSO_4 solution.

of the beta radiation from the S^{35} . The investigation was carried out in the specially constructed apparatus which is pictured in Fig. 6.

For the determination of the dose rate received by the catalyst, special experiments were set up in which a model vessel was used which had the same form and dimensions as the reactor. The design of the experiment for dosimetry of the electron beam is shown in Fig. 7. While the experiments on ferrous sulfate dosimetry were being carried out, the current which impinged on the ionization chamber monitor was simultaneously measured. The depth of the layer of the dosimetric solution (2 cm) was known to exceed the depth of the layer of complete absorption of 800 kev electrons. In Table 2 the values of the dose rate are given (ev/sec for 1 ml of the dosimetric solution) as a function of the current to the chamber. For the experiments carried out in the quartz reactor, the constancy of conditions of irradiation and the value of the dose rate were established by the value of the current to the chamber monitor. For evaluation of the dose rate received by the catalyst layer it was assumed that the thickness of the layer of the solid catalyst guaranteed complete absorption of the electron stream. The catalyst, receiving a dose of the order of 1.4×10^{20} - 2.5×10^{20} ev/ml, became warm, so that even with the use of an impulse thermoregulator, an increase of the temperature in the reactor of 2-3° was observed.

The products of the reaction were fractionated. Cyclohexene (b.p. 82.5°, n_D^{20} 1.4470; d_4^{20} 0.8119), water and unreacted cyclohexanol were separated. Isomerization and polycondensation products were not observed. An investigation of the infra-red spectra confirmed the presence of cyclohexene in the catalyzate.

The results of the kinetic experiments are given in Fig. 8. The data obtained indicate that in contrast to the beta irradiation from the radioactive isotopes, external irradiation of the catalyst with fast electrons did not cause any noticeable change in its catalytic properties for the given reaction.

Discussion of the Results of the Experiments

1. Not only radioactive sulfur, but also radioactive calcium increases the catalytic activity of magnesium sulfate in the dehydration reaction of cyclohexanol. For this effect, the radioactive isotope absolutely must be a component part of the catalyst being used. It is reasonable to propose that the increased activity of the radioactive catalyst studied is connected with the continuous bombardment of the active centers of the catalyst by beta particles. The latter transfer their energy to the adsorbed molecules of cyclohexanol and decrease the activation energy of the chemical reaction.

2. In proportion to the disintegration of the isotope which is in the catalyst, there is a decrease in the catalytic activity. Consequently, the new elements which are formed by the radioactive transformation do not play a promoting role. The bombardment of the surface of the catalyst with fast electrons during the time of the reaction does not produce a noticeable change of catalytic properties of the magnesium sulfate. Obviously the activation of the surface of the catalyst due to the radioactive radiation itself is more effective.

SUMMARY

1. The action of radioactive catalysts on the dehydration of cyclohexanol was investigated; the catalysts used were $MgSO_4$ with Na_2SO_4 containing S^{35} and $MgSO_4$ with $CaCl_2$ containing Ca^{45} .
2. The increase of catalytic activity of the radioactive catalysts in comparison with the non-radioactive, which was discovered earlier by the same authors, was confirmed by a large number of facts.
3. The catalytic activity decreased in proportion to the loss of radioactivity of the catalyst as a consequence of the disintegration of the radioactive S^{35} and Ca^{45} .
4. The bombardment of the surface of the non-radioactive catalyst with fast electrons (800 kev) did not give a noticeable effect, in contrast to the action of beta particles from S^{35} or Ca^{45} which were introduced into the composition of the catalyst.

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MECHANISM OF CONTACT CONVERSIONS OF CERTAIN ORGANIC SUBSTANCES IN THE PRESENCE OF α -IRON

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It is well known that iron has a strong tendency toward the formation of organic complexes [1, 2] and does not give [3] organometallic compounds of the type R_2FeHal and $RFeHal_2$, where $R = Ar, Alk$. Organometallic compound formation also is not observed in contact conversions of alkyl halides in the presence of α -iron [4]. There have been reported [5] and isolated carbonyls, cyanides, and substituted carbonyls, cyanides, and substituted carbonyls [3] of iron, having an iron-carbon bond of an unusual character. There are grounds for assuming that iron possesses a weak chemical affinity for carbon, which is manifested in the low value of the bond [energy] Q_{Fe-C} , which has not yet been determined by thermochemical or other methods [6]. No success was met in determining Q_{Fe-C} by a kinetic method [7], since the cubic body-centered α -iron does not dehydrogenate cyclohexane or its homologs; this is explained by the multiplet theory [8] by a geometric factor: the absence of a [111] face, which has elements of symmetry with a molecule reacting according to a sextet mechanism. According to the work of Kiperman and Balandin [9], the magnitude of Q_{Fe-C} was calculated as 19.1 kcal/mole.

According to the doublet mechanism [10] *n*-butane is not dehydrogenated in the presence of α -iron [11]; under such conditions Hagg [12] observed cracking of the original material and the formation of a carbide.

In the literature there are reported [13, 14] inclusion structures of iron (carbides [15], carbonitrides, and nitrides [16, 17]) that are the technical importance, in which the metal manifests a tendency toward formation of a continuous series of solid solutions and forms phases of varying composition from MeX to Me_nX . Iron carbides are formed in metallurgy, in the synthesis using CO and H_2 [18], and also on the interaction of saturated hydrocarbons with reduced ammonia-synthesis catalysts [19]. We detected the low-temperature carbide Fe_2C [20] in the dehydrogenation of propanol-2 in the presence of iron reduced from the oxalate or oxide. At increased temperatures iron interacts with sulfur, forming reduced structures [14] of varying composition FeS_{1+x} , where $0 \leq x \leq 1$. The magnetic properties of such systems are very sensitive to changes in the amount of sulfur and can be characterized by the change in magnetic susceptibility [21-24].

In hydrotreating high-sulfur petroleum, there is observed the formation of sulfides of the metals present in the catalyst compositions [25-28]. With a view to studying the mechanism of desulfurization in the presence of iron catalysts, we studied [29] the model reaction of the conversions of di-*n*-butyl sulfide on α -Fe. In the work it was established that in addition to the basic process of sulfur removal there are observed redistribution of hydrogen and cracking of the material, but no formation of other organic sulfur compounds; hydrogen sulfide is formed on prolonged contact, when the catalyst activity is reduced owing to complete fixation of sulfur on the catalyst. The spent catalysts contained sulfur in the form of free sulfur and that dissolved in pyrrhotin.

In the presence of hydrogen the main direction of the process takes place according to the index $\begin{smallmatrix} \geq C & H \\ -S & H \end{smallmatrix}$ of hydrogenolysis of the $\geq C-S-$ bond with the formation of hydrogen sulfide, which interacts with the metal surface. A simultaneous possibility is the hydrogenolysis of the $\geq C-C\equiv$ bond with the formation of methane and saturated hydrocarbons according to the index $\begin{smallmatrix} \geq C & H \\ \geq C & H \end{smallmatrix}$. Hydrogen restores the surface of the catalyst, hydrogenating the sulfur and regenerating the active centers of the catalyst.

In our studies it was established [11, 29] that cubic body-centered iron possesses the capability at temperatures above 200° to embed atoms of sulfur or carbon, breaking them from the organic molecules, with the formation of

carbide or sulfides with nonstoichiometric ratios of sulfur. The formation of these new phases of the catalyst is accompanied by deep disintegration of the molecules, with the evolution of hydrogen and the formation of hydrocarbon fragments of C_1 , C_4 , traces of C_2 and C_3 .

Values of ϵ , the apparent activation energy, calculated from kinetic data [11, 20, 29], were utilized in the present work for plotting groups of vulcanic origin [30]. The table shows ϵ , and also E (energy barriers) and q (adsorption potentials) for the dehydrogenation of propanol-2 and the contact conversions of di-n-butyl sulfide in

Apparent Activation Energies ϵ , Energy Barriers E , and Adsorption Potentials q in kcal/mole

Catalyst	Dehydrogenation of (CH_3) ₂ CHOH S/2 = = 203.6; U/2 = -5.9				Decomposition of n-(C_4H_9) ₂ S S/2 = = 153.5; U/2 = -7.3			
	q	$-E$	ϵ found in work calc. per [36]		q	$-E$	ϵ found in work calc. per [36]	
α -Fe	195,2	14,3	10,7		147,5	13,3	10,0	
α -Fe, Fe ₂ C (30%)	184,6	24,9	18,7	19,0				
α -Fe, carbided by n-butane	185,8	22,7	17,0	17,85 17,64 16,89 16,02	Was inactive			
α -Fe, Fe ₂ C, reduced by hydrogen	194,8	14,7	11,0					
α -Fe, FeS _{1+x} , reduced by hydrogen					143,9	16,9	12,7	
α -Fe, sulfided by n-butyl mercaptan					134,5	26,3	19,7	19,1
Catalyst according to [31]	182,9	26,6	20,0					

the presence of iron. In Fig. 1 (curve I) there is shown the depressed curve for the dehydrogenation of propanol-2. In proportion to the accumulation of carbide the catalyst activity decreases and the energy barrier of the reaction and the activation energies increase, as shown graphically by the secants FN. The section F_1N_1 corresponds to freshly reduced α -Fe; F_2N_2 corresponds to that containing carbide. The secant F_3N_3 , the furthest removed from Z, the peak of the curve, corresponds to the iron catalyst investigated in the work of Balandin and Teteni [31]. As is evident from Fig. 1 (Curve II), in proportion to the accumulation of sulfur the activity of the catalyst decreases: The secant NF is removed from Z (the peak of the curve), the energy barrier increases, and the decomposition is halted.

Originating from the energetic and structural representations of [32], a possible mechanism of the contact conversions of organic substances on α -Fe is examined, below.

According to the multiplet theory [30], active centers exist on the surface of a catalyst; in order to transfer atoms into the surface, it is necessary to use part of the energy of sublimation λ_1 .

$$Q_{A-K_{true}} = Q_{A-K_{lat}} + \lambda_i,$$

where λ_i is the sublimation term, which may be positive or negative, in accordance with

$$\lambda_i = \alpha\lambda_K - \lambda_{A-K} + \lambda_{A-K, K_{lat}},$$

where α is a fraction ($0 < \alpha < 1$), equal to 0.5 for a smooth surface; λ_K is the sublimation energy of an atom of K in the lattice; λ_{A-K} is the sublimation energy of the multiplet complex A-K; $\lambda_{A-K, K_{lat}}$ is the sublimation energy of the surface complex A-K where K is bound to the entire lattice K_{lat} . A change in the number of neighbors in the surface (microroughness) of the catalyst influences the entire sublimation term λ_i .

An atom of the metal Z located in the body of the cube is exposed and becomes a surface atom if one or more neighboring atoms are missing from the cell. Figure 3 represents a defect lattice, where the atom is surrounded by 5 and 6 neighboring atoms, i.e., λ_i differs in magnitude. In such a [110] plane there are no longer holes* at the

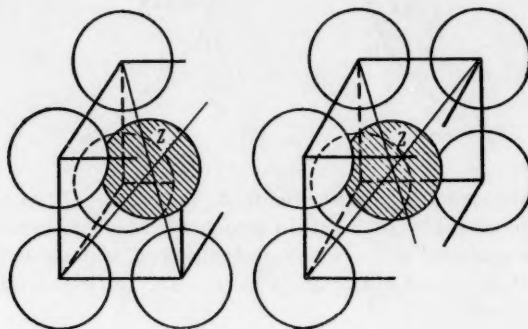


Fig. 3. Defect lattice of α -Fe (Fe_6 , Fe_5).

faces of the cube, even though there is retained the openness of the lattice which attends the cubic system. On superposition of a reacting molecule on an active center (Fig. 4), contact conversion of the alcohol is possible, with the formation of acetone and hydrogen. It is possible that these centers have a lowered but more stable activity.

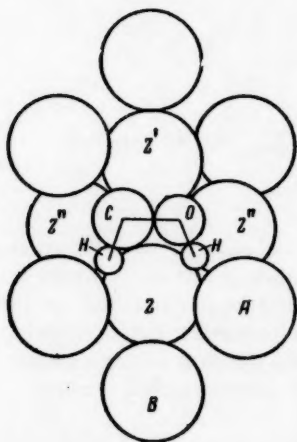


Fig. 4. Graphical representation of defect surface of α -Fe and index group on it.

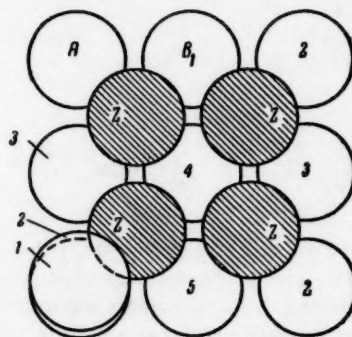


Fig. 5. Structure of active center of α -Fe (Fe_6 , Fe_4).

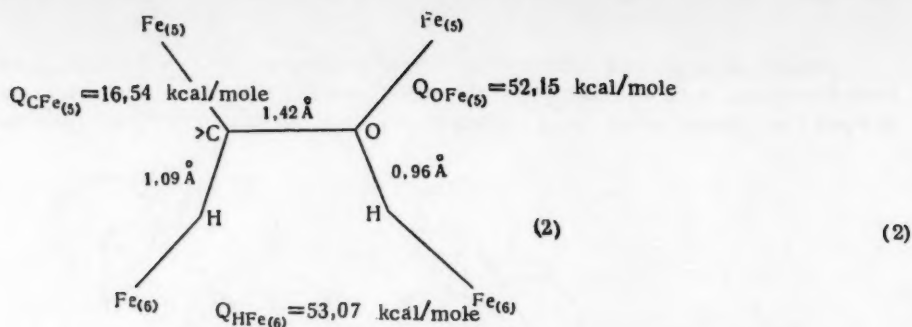
These fine differences in the microstructure of the catalytic surface are manifested in the values of $Q_A - K$ (where $A = C, O, H$) and depend on λ_i .

In [36] Matyushenko takes into consideration the change in energy of the bond $Q_A - K$ in relation to n_K , the number of neighbors of the surface atom of the catalyst (which corresponds to differing λ_i). Knowing the magnitude of the activation energy ϵ , which is determined from experimental data, one can find E and compare it with the E which is calculated according to the equation

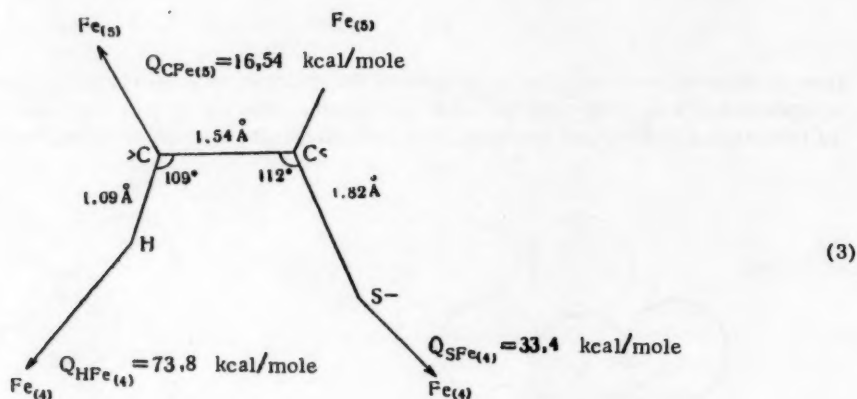
$$E = -Q_{C-H} - Q_{O-H} + Q_{O-Fe} + Q_{C-Fe} + 2Q_{H-Fe},$$

in which the magnitude of $Q_A - K$ is calculated according to [36]; one can then find on what active centers of the α -Fe the catalytic dehydrogenation of the alcohol to acetone takes place.

The calculation which was carried out showed that in the dehydrogenation of the alcohol the atoms responsible are those surrounded by 5 and 6 neighboring iron atoms (Fe_5 , Fe_6) with $\alpha = 3/4$ (scheme 2).



The structure of the active center is presented in Fig. 5; the atoms of Z are surrounded by 4 and 5 neighbors. Such atoms possess an increased unsaturation. From the model it follows that free access to such an iron atom is available for an organogen, for example, sulfur, which is chemisorbed, with the formation of iron sulfide. Calculation shows that with superposition of di-n-butyl sulfide on α -Fe ($\epsilon = 19.7$ kcal/mole) the $\text{Fe}_{(4)}$ and $\text{Fe}_{(5)}$ iron atoms prove to be the most active (scheme 3).



It has been established experimentally that accumulation of carbon and sulfur in the α -Fe lattice poisons the catalytic surface. The low-temperature labile formations of carbide or sulfide or iron can be hydrogenated, with the formation of saturated hydrocarbons and hydrogen sulfide and the regeneration of the α -Fe. The imbedment of oxygen, with the formation of hexagonal ferric oxide, changes its catalytic properties. Iron oxide dehydrogenates and dehydrates alcohols [37], but it does not give carbides and sulfides, even though it retains a marked ability for cracking hydrocarbon radicals of molecules, with the formation of X-ray-amorphous carbon or sulfur.

SUMMARY

1. The mechanism of the contact conversions of propanol-2 and di-n-butyl sulfide in the presence of α -Fe has been discussed.
2. On the basis of kinetic data for the dehydrogenation of propanol-2 and the decomposition of di-n-butyl sulfide, the energy barriers E and the adsorption potentials q have been found.
3. A space model has been proposed for the active centers of α -Fe, and also the energy schemes of the index groups of the reactions studied have been analyzed.

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CATALYTIC DEHYDROGENATION OF n-PENTENES

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It is of considerable interest to study the reaction of catalytic dehydrogenation of normal-structure pentenes for the purpose of obtaining piperylene from the products of petroleum cracking and processing. Piperylene can be utilized as a monomer for synthetic rubber production. According to the literature data [1], on copolymerizing piperylene with other vinyl compounds a rubber is obtained which has considerable abrasion resistance. By catalytic dehydrocyclization, piperylene can be converted into cyclopentadiene [2], which because of its high reactivity is utilized for the synthesis of a number of substances, for example, insecticides.

According to the literature data [3], piperylene can be prepared from hydrocarbons, oxygen-containing compounds, halogen derivatives, and amines. As described in [4], on passing pentene-2 over alumina-chromium catalyst at 600° with 0.4 sec contact time at a reduced pressure of 190 mm Hg, piperylene was obtained with a yield of 30.3% based on the pentene throughput, at a conversion of 44%. The process is accompanied by considerable carbon deposition on the catalyst, ~7.6 wt. %. According to patent data [5], on dehydrogenating pentene-2 on a mixed oxide catalyst (75 parts MgO, 20 parts Fe₂O₃, 5 parts CuO, and 5 parts K₂O, by weight) at 650°, feed rate 0.498 hr⁻¹, and water vapor dilution in 1: 7.6 molar ratio, the yield of pentadienes, mainly piperylene, is 26.8%, along with the formation of 33.4% butadiene based on the hydrocarbon reacting. As indicated in a patent [6], pentene-1 gives the highest yields of piperylene. The process is carried out in two stages. In the first stage pentane dehydrogenation is carried out at 560° in the presence of chromic oxide on bauxite. The degree of conversion is about 30%; then a second dehydrogenation is performed on the resulting mixture of pentenes and unreacted pentane. According to another patent [7], pentane dehydrogenation is carried out on black chromic oxide obtained by the thermal decomposition of chromic salts. The mixture of hydrocarbons obtained in the first stage is passed without separation over granular aluminum oxide containing about 15% chromic oxide. Product yields are not indicated. Tishchenko [8], on passing 2,3-dichloropentane and 1,4-dichloropentane over a catalyst consisting of SiO₂ and MgCl₂ or CuCl₂ at 300°, obtained piperylene with yields of 67 and 43.5% respectively.

Piperylene is formed in small quantity as a by-product in the production of butadiene from ethyl alcohol by the Lebedev method [9]. The catalytic splitting of the acetate of 1,2-pentanediol at 550-570° gives piperylene with a 60-65% yield [10]; similar results are given by the dehydration of certain pentanediols [11].

In the present work a study was made of the conditions for conducting the reaction of dehydrogenation of n-pentenes to piperylene, and of the reaction kinetics.

EXPERIMENTAL

The experiments were carried out by a flow method with water vapor dilution on a 4 ml of quantity of mixed oxide catalyst. The apparatus [12] and experimental method have been described previously [13]. The reaction products leaving the reactor passed into a receiver fitted with a reflux condenser, where the water vapor was condensed; the catalyzate [product of catalysis] was collected in a trap chilled by dry ice-acetone in a Dewar flask. The off-gas was collected in a gas-holder over saturated salt solution. The gas volume was reduced to normal conditions (NTP). The collected gas was analyzed in a modified Orsat apparatus and, in a number of experiments, by a chromatographic method. The amounts of CO₂, total unsaturated hydrocarbons C₃ and C₄, ethylene, hydrogen, and saturated hydrocarbons were determined on the off-gas. The catalyzate was analyzed for content of piperylene and unreacted pentenes.

Piperylene was determined in the gas phase with maleic anhydride. A weighed sample of the catalyzate was evaporated in a stream of nitrogen into a graduated cylindrical gas-holder over saturated salt solution. The hydrocarbon concentration in the gas mixture did not exceed 15-16%, in order to avoid condensation. This method is successful in preferentially determining trans-piperylene, since cis-piperylene is almost entirely unreactive with maleic anhydride under these conditions, as is well known from the literature [14, 15] and verified by us on synthetic mixtures. The total of cis- and trans-piperylene was determined in the liquid phase. A weighed sample of the catalyzate was introduced into a solution of maleic anhydride in toluene and allowed to stand for 24-30 hours. The excess maleic anhydride was converted to the acid, which was determined iodometrically.

The initial hydrocarbons were prepared by the dehydration of n-amyl alcohol over alumina and were purified by distillation in a 60-theoretical-plate column. A mixture of n-pentenes was obtained, consisting of 72% pentene-1 and 28% pentene-2 (d^{20}_4 0.6435; n^{20}_D 1.3748).

The experiments were carried out with dilution of the pentenes by water vapor in the ratio 1: 2.4-3.6 parts by weight. The influence of temperature and feed rate on piperylene yield was investigated.

TABLE 1. Catalytic Dehydrogenation of n-Pentenes (dilution with water vapor in the ratio of 1: 2.6-3.5 by weight)

Temp., °C	Feed rate, hr ⁻¹	Yield of C ₈ H ₈ , wt. % (trans-pi- perylene)	Gas analysis, vol. %				
			CO ₂	C ₃ +C ₄	C ₂ H ₄	H ₂	C _n H _{2n+2}
540	2,96	9,0	5,0	1,8	3,3	78,2	11,7
540	3,90	9,3	8,5	1,3	2,8	85,0	7,5
560	3,02	10,2	6,1	2,1	5,2	72,8	14,4
560	3,45	15,0	5,2	1,6	5,0	75,0	13,3
560	4,50	13,8	4,9	1,3	4,8	75,4	13,6
560	5,88	13,0	3,4	1,0	3,4	78,4	13,8
560	7,30	10,0	3,5	1,2	3,5	80,4	11,4
560	8,60	8,0	3,2	1,0	2,4	82,3	11,5
580	3,66	16,0	7,3	2,1	6,2	67,7	16,7
580	4,86	17,1	5,8	2,6	5,8	71,2	13,6
580	5,90	17,2	5,5	1,8	5,1	75,4	12,2
580	6,64	17,4	4,7	2,0	5,3	76,4	11,6
580	8,00	10,3	3,8	1,4	4,3	79,0	11,5
600	4,00	19,2	7,9	2,7	9,6	60,5	18,3
600	4,82	19,4	7,9	3,5	8,4	63,2	17,0
600	5,45	20,0	7,4	2,6	8,0	64,9	17,1
600	7,20	20,2	6,9	2,3	6,4	68,2	17,2
600	8,00	17,4	6,4	0,4	6,4	75,5	11,3
620	4,15	19,3	8,6	3,7	10,9	58,2	18,6
620	4,75	21,0	8,8	3,2	10,8	60,3	16,9
620	5,78	19,6	8,8	3,8	9,2	60,8	17,4
620	8,05	18,2	8,8	2,8	8,1	66,0	14,3
640	5,76	21,4	9,4	4,4	12,2	56,3	17,7
640	7,45	22,0	7,9	4,0	13,8	56,9	17,4

Influence of Temperature. Experiments were conducted in the temperature interval 540-640° with pentenes feed rate 4.5-5 liters per liter of catalyst per hour. It was found that the yields of trans-piperylene (piperylene content in these experiments was determined by maleic anhydride) on increasing the temperature from 540 to 600° increases from 9 to 20%. With a further increase in temperature to 640° in piperylene yields remain unchanged, and simultaneously there is an increased formation of CO₂ and light hydrocarbons (cracked products). The data obtained are shown in Table 1.

Influence of Feed Rate. The pentenes feed rate was varied from 3 to 8 liters (hr⁻¹). At a feed rate of 5.5-6 hr⁻¹ the yields of trans-piperylene constitutes 13-15% at 560° and 17% at 580°. On increasing the feed rate to 7-8 hr⁻¹ at those same temperatures, the yields are reduced to 8-10%. An increase in feed rate to 8 hr⁻¹ at 600° affects to a lesser degree the yields of trans-piperylene, which are reduced altogether only 2.5-3% (Fig. 1). The composition of the off-gas at 580° in relation to the feed rate is shown in Fig. 2.

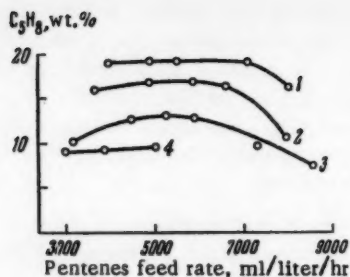


Fig. 1. Yields of trans-piperylene in relation to pentenes feed rate: 1) At 600°; 2) at 580°; 3) at 560°; 4) at 540°.

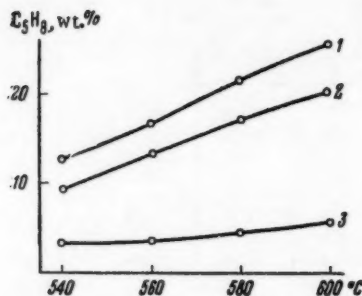


Fig. 3. Yields of piperylenes in relation to temperature: 1) Total of cis- and trans-piperylene; 2) trans-piperylene; 3) cis-piperylene.

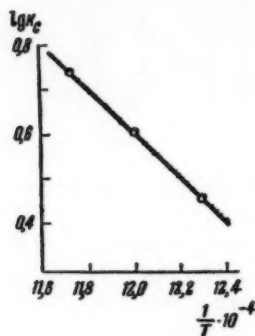


Fig. 5. Relation between $\log k_c$ and reciprocal of absolute temperature.

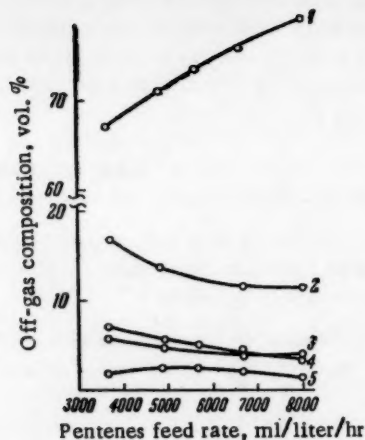


Fig. 2. Composition of off-gas in relation to pentenes feed rate, at 580°: 1) H_2 ; 2) C_nH_{2n+2} ; 3) C_2H_4 ; 4) CO_2 ; 5) C_3 and C_4 .

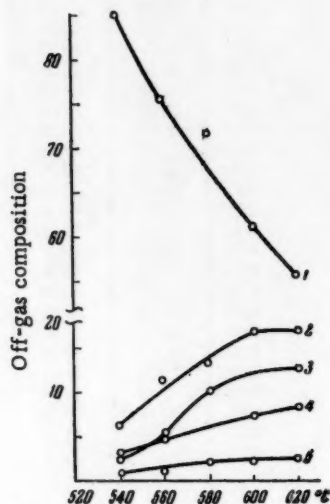


Fig. 4. Composition of off-gas in relation to temperature, at pentenes feed rate 4.8 hr^{-1} : 1) H_2 ; 2) C_nH_{2n+2} ; 3) C_2H_4 ; 4) CO_2 ; 5) C_3 and C_4 .

For determining the total yield of piperylene of the cis- and trans-forms, experiments were conducted in that same temperature interval, 540-640°, with feed rate 5.5 hr^{-1} . The piperylene yields based on the pentenes throughout constitute 12.3% at 540° and 25.6% at 600°. Figure 3 shows the change in piperylene yields in relation to temperature.

The composition of the off-gas in relation to temperatures is shown in Fig. 4. Thus, on the basis of the data obtained, one can come to the conclusion that the most favorable conditions for dehydrogenating n-pentenes to piperylene are a temperature of 580-600°, feed rate $4-5.5 \text{ hr}^{-1}$, and dilution with water vapor 1: 2.6 to 1: 3.2 parts by weight. The

piperylene yields under these conditions constitute 21.6 and 25.6 wt. % respectively, based on the n-pentenes throughout, with ratio of cis- to trans-forms of piperylene equal to 1: 4.

Kinetics of n-Pentenes Dehydrogenation. Experiments were conducted in the temperature interval 540-580°, feed rate 5.5 hr⁻¹, and dilution with water vapor in ratio 1: 11.6 moles. Under these conditions the reaction proceeds with minor formation of by-products of decomposition, and the catalyzate yield constituted 98-98.5%.

For determining the relative adsorption coefficients of the reaction products, dehydrogenation rates were measured for binary mixtures of n-pentenes with the reaction products (piperylene and hydrogen) [16]. As in the case of isopentenes dehydrogenation [17], the relative adsorption coefficient of hydrogen, found equal to 0.8, does not change with temperature. The adsorption coefficient of piperylene depends on temperature, decreasing with an increase in temperature. Thus, at 540° z_2 is 5.3, and at 580° it is reduced to 3.35 (Table 2).

TABLE 2. Relative Adsorption Coefficients of Piperylene (feed rate 5.00 hr⁻¹, dilution with water vapor 1: 3 by weight)

Temp., °C	Comp. of mixture, mole %		Piperylene obtained, ml in 5 min	z_2	Temp., °C	Comp. of mixture, mole %		Piperylene obtained, ml in 5 min	z_2
	C ₅ H ₁₀	C ₅ H ₈				C ₅ H ₁₀	C ₅ H ₈		
540	100	—	41,1		580	100	—	72,4	
540	77,8	22,2	16,4	5,3	580	77,8	22,2	36,7	3,35
560	100	—	55,2		600	100	—	85,5	
560	77,8	22,2	25,1	4,2	600	77,8	22,2	48,4	2,7

TABLE 3. Rate Constant k_c and Thermodynamic Functions of Adsorptive Displacement

Temp., °C	Rate constant, ml. min	z_2	$-\Delta F$, cal	ΔH , kcal/mole	ΔS , cal/°C/mole
540	2,92	5,3	2690		22,5
560	4,06	4,2	2370	15,7	22,2
580	5,55	3,35	2046		20,8

For calculating the reaction rate constant for the dehydrogenation of n-pentenes from the experimental data, there was applied the general kinetic equation of mono-molecular catalytic reactions in a flow system [18], based on the equation:

$$\frac{dx}{dt} = k \frac{[A_1]}{[A_1] + z_2 [A_2] + z_3 [A_3]} \quad (1)$$

As had been pointed out previously [19], the water-vapor diluent does not enter into this equation, since it reduces the partial pressure of the hydrocarbon and does not exert any influence on the reaction rate. Reaction rate constants calculated by Eq. (1) are shown in Table 3. The logarithmic relationship between the reaction rate constant and the reciprocal of absolute temperature is shown in Fig. 5. The points fall on a straight line; the Arrhenius equation is fulfilled. The activation energy, calculated from the reaction rate constants, is found equal to 21.3 kcal/mole; the pre-exponential multiplier is equal to 6.23. From the values found for the relative adsorption coefficients, there were calculated the changes in free energy, heat content, and entropy of adsorptive displacement from the active centers of the catalyst (Table 3).

SUMMARY

1. The dehydrogenation of n-pentenes on an oxide catalyst has been studied. Under optimum conditions' the yields of piperylene reach 25%.
2. The kinetics of dehydrogenation of n-pentenes to piperylene have been investigated. Reaction rate constants and thermodynamic functions of adsorptive displacement on the oxide catalyst have been determined.

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KINETICS OF DEHYDROGENATION AND DEHYDRATION OF ALCOHOLS AND DEHYDROGENATION OF HYDROCARBONS ON WS_2 AND MoS_2 CATALYSTS

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Many papers and patents have been concerned with the study of the catalytic properties of tungsten sulfides and molybdenum sulfide. These compounds are used in industry both in the pure form and in mixtures with other compounds as catalysts for degradative hydrogenation at high pressures and high temperatures [1-4]. An advantage of the sulfide catalysts is their low sensitivity towards contact poisons, especially to sulfur, which permits use of these catalysts for hydrosulfurization, and their operation for a long time [4-6]. The crystal lattices of WS_2 and MoS_2 possess almost identical structures. They consist of two-dimensional layers bound by weak van der Waals forces and each such layer in its turn consists of three layers: a layer of metal atoms surrounded on two sides with sulfur atoms, where the forces in this latter layer are covalent. The lattice parameters are quite close: for WS_2 $a = 3.18$; $c = 12.5$ Å and for MoS_2 $a = 3.15$; $c = 12.30$ Å. For such catalysts of similar structure it is of interest to study the kinetics of a series of reactions of atmospheric pressure in a flow system and to determine the C, H and O bond energies with these catalysts. With this aim the kinetics were studied of the dehydrogenation and dehydration of ethyl, n-propyl and isopropyl alcohols and the dehydrogenation of cyclohexane and cyclohexene on WS_2 , and the activation energies of these reactions and the relative adsorption coefficients of propylene and water were determined. On MoS_2 the activation energies of dehydrogenation and dehydration of isopropyl alcohol and dehydrogenation of cyclohexene were determined.

EXPERIMENTAL

Experiments were conducted using the industrial sample WS_2 No. 3, obtained from the IOKh AN SSSR laboratory for investigation of catalysts. The physicochemical properties of this sample were given detailed study by Samoilov and Rubinshtein [7]. We ourselves prepared the MoS_2 . For comparison WS_2 No. 1 was also prepared. The catalysts were prepared according to the usually prescribed preparation of industrial WS_2 catalyst [4]. An ammoniacal solution of ammonium tungstate (molybdate) was saturated with hydrogen sulfide. The precipitated crystals of ammonium thiotungstate (thiomolybdate) were transferred under a nitrogen atmosphere into a quartz tube and reduced with hydrogen at 400° until hydrogen sulfide ceased to be evolved (checked with cadmium acetate). The kinetic experiments were carried out in the usual flow-through apparatus adopted in our laboratory. The liberated gaseous products were collected at atmospheric pressure in a Patrikeev automatic gasometer system and analyzed on the VTI gas-analyzer. Since the gaseous unsaturated products were appreciably soluble in the catalyzate, their quantity in the catalyzate was determined by Kaufman-Vinograd bromine values and by calculation the appropriate correction was added. The reactor temperature was maintained with an accuracy of 0.5° and was measured by means of a chromel-aluminum thermocouple using the compensation method. The materials were subjected to careful purification and possessed the following constants: ethyl alcohol: b.p. 78.0° ; d_4^{20} 0.7895; n_D^{20} 1.3612; n-propyl alcohol: b.p. 97.0° (746 mm); d_4^{20} 0.8060; n_D^{20} 1.3854; isopropyl alcohol: b.p. $81-81.5^\circ$ (734 mm); d_4^{20} 0.7858; n_D^{20} 1.3782; cyclohexane: b.p. $79.5-80.0^\circ$ (752 mm); d_4^{20} 0.7785; n_D^{20} 1.4262; cyclohexene: b.p. $82.5-83.0^\circ$ (756 mm); n_D^{20} 1.4465; d_4^{20} 0.8100.

Dehydrogenation and Dehydration of Alcohols on WS_2 No. 3 and WS_2 No. 1

Ethyl Alcohol. Experiments were conducted in the $209-258^\circ$ temperature range on the industrial sample WS_2 No. 3. In the gaseous products there was present, besides hydrogen and unsaturated compounds, a considerable quantity

of CO₂ and saturated hydrocarbons. The carbon value of the saturated material was close to 2. In the calculation of the activation energy of dehydrogenation a correction was inserted for the quantity of hydrogen consumed in hydrogenation of the unsaturated hydrocarbons. The results are given in Table 1. The apparent activation energy of dehydrogenation was $\epsilon_{H_2} = 18.3$ kcal/mole, of dehydration $\epsilon_{H_2O} = 21.6$ kcal/mole.

n-Propyl Alcohol. Experiments were conducted in the 170-220° temperature range on the industrial sample WS₂ No. 3. In the gases, besides hydrogen and unsaturated materials, was detected a considerable quantity of CO₂ and saturated hydrocarbons. In calculating the activation energy the quantity of hydrogen consumed in hydrogenation of the unsaturated material and methyl radicals was disregarded. The apparent activation energy of dehydrogenation $\epsilon_{H_2} = 9.4$ kcal/M and of dehydration $\epsilon_{H_2O} = 13.9$ kcal/M. The results are given in Table 2.

TABLE 1. Dehydrogenation and Dehydration of Ethyl Alcohol. WS₂ No. 3; volume 5 ml;

$l = 2$ cm; feed rate $A_1 = 52.8$ ml/min; $\epsilon_{H_2} = 18.3$ kcal/mole; $\frac{\epsilon_{H_2}}{\lg k_0} = 2.50$; $k_0 = 3.0 \cdot 10^7$; $\epsilon_{H_2O} = 21.6$ kcal/mole; $\frac{\epsilon_{H_2O}}{\lg k_0} = 2.30$; $k_0 = 2.4 \cdot 10^9$; \underline{m} in ml/min · ml cat. NTP

Temperature, °C	$V, \frac{\text{ml}}{\text{min NTP}}$	Gas analysis in %				Dehydrogenation				Dehydration			
		CO ₂	C _n H _{2n}	H ₂	C _n H _{2n+2}	m_{H_2}	$\lg k_0$	ϵ_{H_2} $\lg k_0$	m_{H_2O} calculated with $\epsilon_{H_2} = 18.3$	$m_{C_nH_{2n}}$	$\lg k_0$	ϵ_{H_2O} $\lg k_0$	$m_{C_nH_{2n}}$ calculated with $\epsilon_{H_2O} = 21.6$
209	2.7	4.3	72.5	14.9	6.2	0.11	7.341	2.50	0.10	0.39	9.381	2.30	0.39
224	4.9	6.1	76.3	12.1	5.5	0.17	7.285	2.51	0.17	0.75	9.375	2.30	0.77
225	5.0	5.8	75.9	11.4	5.9	0.17	7.278	2.52	0.18	0.76	9.381	2.30	0.77
228	6.2	7.0	77.5	9.2	6.2	0.19	7.254	2.52	0.21	0.96	9.397	2.30	0.94
239	8.9	3.4	74.2	10.8	6.1	0.30	7.234	2.51	0.31	1.32	9.327	2.32	1.51
244	11.1	7.2	76.1	12.4	4.1	0.36	7.301	2.51	0.36	1.69	9.368	2.31	1.76
247	14.8	8.4	76.5	9.7	5.3	0.44	7.324	2.50	0.42	2.26	9.414	2.29	2.12
247	14.9	—	—	—	—	0.45	7.333	2.50	0.42	2.28	9.418	2.29	2.12
247	14.6	9.1	76.0	10.0	4.9	0.43	7.313	2.50	0.42	2.22	9.406	2.29	2.12
258	21.4	8.8	77.2	8.0	6.0	0.60	7.308	2.50	0.59	3.30	9.408	2.29	3.10

TABLE 2. Dehydrogenation and Dehydration of n-Propyl Alcohol. WS₂ No. 3; volume

5 ml; $l = 2$ cm; feed rate $A_1 = 54.2$ ml/min; $\epsilon_{H_2} = 9.4$ kcal/mole; $\frac{\epsilon_{H_2}}{\lg k_0} = 2.63$; $k_0 = 4.17 \cdot 10^3$; $\epsilon_{H_2O} = 13.9$ kcal/mole; $\frac{\epsilon_{H_2O}}{\lg k_0} = 2.22$; $k_0 = 1.8 \cdot 10^6$; \underline{m} in ml/min · ml cat. NTP

Temperature, °C	$V, \frac{\text{ml}}{\text{min NTP}}$	Gas analysis in %				Dehydrogenation				Dehydration			
		CO ₂	C _n H _{2n}	H ₂	C _n H _{2n+2}	m_{H_2}	$\lg k_0$	ϵ_{H_2} $\lg k_0$	m_{H_2O} calculated with $\epsilon_{H_2} = 9.4$	$m_{C_nH_{2n}}$	$\lg k_0$	ϵ_{H_2O} $\lg k_0$	$m_{C_nH_{2n}}$ calculated with $\epsilon_{H_2O} = 13.9$
172	2.1	8.4	62.0	23.8	5.8	0.10	3.610	2.61	0.10	0.26	6.225	2.23	0.28
179	2.6	8.8	63.5	21.1	6.6	0.11	3.581	2.63	0.11	0.33	6.233	2.23	0.35
183	3.1	8.2	65.2	19.4	7.2	0.12	3.579	2.63	0.12	0.41	6.262	2.22	0.41
188	3.7	7.0	68.9	17.1	6.5	0.13	3.564	2.64	0.13	0.51	6.288	2.21	0.48
188	3.7	6.8	68.9	18.8	5.5	0.14	3.596	2.62	0.13	0.51	6.28	2.21	0.48
200	4.9	9.9	65.4	18.4	6.3	0.18	3.600	2.61	0.17	0.65	6.248	2.23	0.70
210	9.7	10.0	69.9	14.0	6.1	0.27	3.506	2.68	0.25	1.36	6.29	2.21	1.25
219	9.3	—	—	—	—	0.26	3.590	2.62	0.25	1.30	6.279	2.22	1.25

Isopropyl Alcohol. Experiments were conducted in the 150-280° temperature range on the industrial sample WS₂ No. 3 and on our prepared catalyst WS₂ No. 1. 98-99% of the gas was absorbed by bromine. The apparent activation energy of dehydration on the industrial sample was $\epsilon_{H_2O} = 17.4$ kcal/mole; on our prepared catalyst 15.8 kcal/mole. The results are given in Tables 3 and 4. The relative adsorption coefficient of the reaction products

on both the samples WS₂ No. 3 and WS₂ No. 1 were determined by the earlier described method [8] for binary mixtures. The calculation was made by means of the formula

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1}, \quad (1)$$

where m_0 is the quantity in ml of unsaturated substances formed during passage of the pure compound; m is the quantity in ml of unsaturated substances formed during passage of mixtures with a p molar alcohol content. The results of determination of z are given in Tables 5 and 6. The true activation energies were calculated from the rate constant, calculated from Balandin's equation [9]

$$k = (z_2 + z_3) A_1 \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1) m, \quad (2)$$

where A_1 is the quantity in ml/min of unsaturated hydrocarbons, which would be formed by complete conversion of the alcohol. z and $m = m_0$ are the same as in formula (1).

TABLE 3. Dehydration of Isopropyl Alcohol. WS₂ No. 3; volume 5 ml; $l = 2$ cm;

feed rate $A_1 = 52.8$ ml/min; $\epsilon_{H_2O} = 17.4$ kcal/mole; ϵ_{H_2O} (true) = 19.3 kcal/mole;

ϵ_{H_2O} (true) = 1.94; $k_0 = 8.65 \cdot 10^9$; m in ml/min · ml cat. NTP

Temper- ature, °C	$m_{C_nH_{2n}}$	k	$\lg k_0$	$\frac{\epsilon_{H_2O}}{\lg k_0}$	k , calcu- lated with $\epsilon_{H_2O} = 19.3$	Temper- ature, °C	$m_{C_nH_{2n}}$	k	$\lg k_0$	$\frac{\epsilon_{H_2O}}{\lg k_0}$	k , calcu- lated with $\epsilon_{H_2O} = 19.3$
149	0,84	0,861	9,935	1,94	0,865	169	2,36	2,764	9,992	1,93	3,060
158	1,33	1,441	9,939	1,94	1,432	175	2,71	3,262	9,924	1,94	3,360
162	1,61	1,608	9,896	1,95	1,765	174	2,70	3,262	9,934	1,94	3,280
166	1,89	2,150	9,932	1,94	2,170	181	3,75	4,458	9,939	1,94	4,430

TABLE 4. Dehydration of Isopropyl Alcohol. WS₂ No. 1; volume 0.5 ml; feed rate

$A_1 = 58.67$ ml/min; $\epsilon_{H_2O} = 15.8$ kcal/mole; ϵ_{H_2O} (true) = 18.3 kcal/mole;

ϵ_{H_2O} (true) = 1.94; $k_0 = 2.78 \cdot 10^9$; m in ml/min · ml cat. NTP

Temper- ature, °C	$m_{C_nH_{2n}}$	k	$\lg k_0$	$\frac{\epsilon_{H_2O}}{\lg k_0}$	k , calcu- lated with $\epsilon_{H_2O} = 18.3$	Temper- ature, °C	$m_{C_nH_{2n}}$	k	$\lg k_0$	$\frac{\epsilon_{H_2O}}{\lg k_0}$	k , calcu- lated with $\epsilon_{H_2O} = 18.3$
213,5	15,06	16,14	9,418	1,94	17,15	224,5	42,20	54,62	9,458	1,93	53,10
220	17,64	19,52	9,421	1,94	20,60	250	48,40	65,47	9,456	1,93	63,70
220	21,26	24,06	9,512	1,94	20,60	256,5	63,32	97,00	9,536	1,94	77,90
229	26,60	31,02	9,442	1,94	31,20	262,5	54,72	77,95	9,351	1,95	96,50
230	27,40	32,18	9,447	1,94	32,00	267	71,00	120,60	9,491	1,93	118,30
238,5	33,86	41,65	9,420	1,94	44,00	267	61,66	93,33	9,380	1,95	118,30

Dehydrogenation of Hydrocarbons on Catalyst WS₂ No. 3

In the experiments with alcohol the catalyst activity fell insignificantly with time. But in working with hydrocarbons the activity fell sharply in the initial experiments after which the fall in activity slowed down and became very small and constant from experiment to experiment. Therefore to obtain comparable results we have had to make a correction for the fall in activity in calculating the activation energy: from the constant fall in activity for different temperatures the fall of activity for a one hour operation of the catalyst was determined and by means of the values of the experimental results were reduced to the activity of the final experiment.

TABLE 5. Relative Adsorption Coefficients of Propylene and Water on the Industrial Catalyst WS₂ No. 3

Propylene				Water			
mole % of alco- hol in mixture	m	z	z _{cp}	mole % of alco- hol in mixture	m	z	z _{cp}
Temperature 150°							
100	4,2	0,76	0,74	104	4,2	0,54	0,56
80	3,5			80	3,7		
100	4,4	0,72		100	4,3	0,58	
60	2,9			70	3,5		
Temperature 163°							
100	8,5	0,73	0,73	100	8,5	0,51	0,52
60	5,7			70	7,0		
100	8,3	0,74		100	8,3	0,54	
80	7,0			80	7,3		
Temperature 170°							
100	11,4	0,72	0,72	100	11,6	0,56	0,57
80	9,6			80	10,0		
100	11,4	0,72		100	11,6	0,59	
60	7,7			170	9,2		
Temperature 180°							
100	15,2	0,78	0,76	100	15,3	0,54	0,52
80	12,9			80	13,5		
100	15,7	0,75		100	15,7		
60	10,5			70	12,9	0,51	

TABLE 6. Relative Adsorption Coefficients of Propylene and Water on the Catalyst WS₂ No. 1

Propylene			Water			Propylene			Water		
mole % of alcohol in mixture	m	z	mole % of alcohol in mixture	m	z	mole % of alcohol in mixture	m	z	mole % of alcohol in mixture	m	z
Temperature 260°						Temperature 173°					
100	33,0	0,70	100	35,0	0,50	100	5,1	0,73	100	5,2	0,56
75	26,7		75	30,0		75	4,1		60	3,9	
100	32,9	0,69	100	34,0	0,50	100	5,1	0,69	100	5,2	0,54
60	22,5		85	31,2		60	3,5		75	4,4	
100	32,5	0,73	100	33,0	0,52	100	5,1	0,65	100	5,2	0,58
90	30,0		60	24,5		75	4,2		85	4,7	
Mean		0,71			0,51	Mean		0,69			0,56
Temperature 200°						Temperature 160°					
100	9,8	0,72	100	10,0	0,50	100	3,6	0,60	100	3,7	0,55
75	7,9		60	7,5		75	3,0		60	2,7	
100	10,0	0,68	100	10,0	0,53	100	3,6	0,66	100	3,7	0,58
90	9,3		75	8,5		60	2,5		75	3,1	
100	10,0	0,70	100	10,0	0,56	100	3,5	0,75	100	3,6	0,50
60	6,8		85	8,9		75	2,8		85	3,3	
Mean		0,70			0,53	Mean		0,67			0,54

Cyclohexane. Experiments were conducted in the 420-490° temperature range. The gaseous products consisted almost entirely of pure hydrogen. There was no more than 2% saturated hydrocarbons at the highest temperatures. The experimental results are given in Table 7. The apparent activation energy of dehydrogenation was $\epsilon_{H_2} = 22.6$ kcal/mole.

TABLE 7. Dehydrogenation of Cyclohexane. WS₂ No. 3; volume 5 ml; *l* = 2 cm; feed rate A₁ = 99.6 ml/min; ε_{H₂} = 22.6 kcal/mole; $\frac{\epsilon_{H_2}}{\log k_0} = 3.33$; k₀ = 6.18 · 10⁶; $\frac{m}{\log k_0}$ in ml · min ml cat. NTP

Temperature, °C	m _{H₂}	lg k ₀	$\frac{\epsilon_{H_2}}{\lg k_0}$	m _{H₂} calculated with ε _{H₂} = 22.6	Temperature, °C	m _{H₂}	lg k ₀	$\frac{\epsilon_{H_2}}{\lg k_0}$	m _{H₂} calculated with ε _{H₂} = 22.6
421	0,43	6,772	3,34	0,45	457	1,05	6,842	3,31	0,94
427	0,52	6,778	3,33	0,54	464	1,14	6,757	3,34	1,23
438	0,73	6,814	3,31	0,70	467	1,15	6,720	3,36	1,35
441	0,74	6,779	3,33	0,76	491	2,02	6,775	3,34	2,09
456	1,06	6,860	3,34	0,91	491	2,00	6,771	3,34	2,09
457	1,04	6,838	3,31	0,94					

TABLE 8. Dehydrogenation of cyclohexane. WS₂ No. 3; volume 5 ml; *l* = 2 cm; feed rate A₁ = 70.6 ml/min; ε_{H₂} = 21.0 kcal/mole; k₀ = 7.33 · 10⁶; $\frac{\epsilon_{H_2}}{\log k_0} = 3.06$; $\frac{m}{\log k_0}$ in ml/min · ml cat. NTP

Temperature, °C	m _{H₂}	lg k ₀	$\frac{\epsilon_{H_2}}{\lg k_0}$	m _{H₂} calculated with ε _{H₂} = 21.0	Temperature, °C	m _{H₂}	lg k ₀	$\frac{\epsilon_{H_2}}{\lg k_0}$	m _{H₂} calculated with ε _{H₂} = 21.0
437	0,21	6,800	3,09	0,25	475	0,56	6,876	3,05	0,53
454	0,35	6,865	3,06	0,35	481	0,60	6,850	3,07	0,60
454	0,33	6,844	3,07	0,35	491	0,73	6,863	3,06	0,72
463	0,48	6,915	3,04	0,42	493	0,79	6,844	3,07	0,75

Cyclohexene. Experiments were conducted in the 437-493° temperature range. The gas analysis results showed that the gas contained almost entirely hydrogen with up to 3% saturated hydrocarbons at the highest experimental temperatures. The experimental results are given in Table 8. The apparent activation energy of dehydrogenation was ε_{H₂} = 21.0 kcal/mole.

Dehydrogenation and Dehydration of Alcohols and Dehydrogenation of Hydrocarbons on MoS₂

Ethyl alcohol underwent dehydrogenation and dehydration of molybdenum sulfide. The reactions are rather complex. Gaseous carbon dioxide, unsaturated hydrocarbons, hydrogen and a considerable quantity of unsaturated hydrocarbons were detected in the reaction gases.

Isopropyl alcohol. Dehydrogenation and dehydration of isopropyl alcohol occurred on molybdenum sulfide. Experiments were conducted in the 170-220° temperature range. The results are given in Table 9. The apparent activation energy of dehydrogenation was ε_{H₂} = 7.4 kcal/mole; of dehydration - 13.6 kcal/mole.

Cyclohexene. Dehydrogenation of cyclohexene occurred without appreciably splitting of the ring. From the gas analysis the quantity of saturated hydrocarbons did not exceed 2% at the highest temperatures. As in the case of dehydrogenation of hydrocarbons on WS₂ No. 1, a correction had to be made here also for the fall in activity. The experimental results are given in Table 10. The apparent activation energy of dehydrogenation of cyclohexenes was 17.7 kcal/mole.

Discussion of Experimental Results

In respect to the dehydrogenation of cyclohexene and cyclohexane, WS₂ No. 3 and MoS₂ displayed similar properties. On both catalysts the reaction proceeded with a low percentage conversion and was accompanied by

TABLE 9. Dehydrogenation and Dehydration of Isopropyl Alcohol. MoS_2 ; volume 5 ml;
 $l = 2$ cm; feed rate $A_1 = 52.8$ ml/min; $\epsilon_{\text{H}_2} = 7.4$ kcal/mole; $\frac{\epsilon_{\text{H}_2}}{\log k_0} = 2.47$; $k_0 = 1 \cdot 10^8$;
 $\epsilon_{\text{H}_2\text{O}} = 13.6$ kcal/mole; $\frac{\epsilon_{\text{H}_2\text{O}}}{\log k_0} = 2.10$; $k_0 = 2.8 \cdot 10^6$; \underline{m} in ml/min ml cat. NTP

Temper- ature, °C	V, ml/min NTP	Gas analysis %				Dehydrogenation				Dehydration			
		CO_2	C_nH_{2n}	H_2	$\text{C}_n\text{H}_{2n+2}$	n_{H_2}	$\lg k_0$	$\frac{\epsilon_{\text{H}_2}}{\lg k_0}$	m_{H_2} cal- culated with $\epsilon_{\text{H}_2} = 7.4$	$m_{\text{C}_n\text{H}_{2n}}$	$\lg k_0$	$\frac{\epsilon_{\text{H}_2\text{O}}}{\lg k_0}$	$m_{\text{C}_n\text{H}_{2n}}$ calculated with $\epsilon_{\text{H}_2\text{O}} = 13.6$
176	5,2	1,5	69,5	25,1	3,9	0,30	3,057	2,42	0,26	0,72	6,437	2,12	0,75
179	5,5	0,8	73,5	24,6	1,1	0,28	3,017	2,4	0,27	0,81	6,463	2,10	0,80
180	5,5	1,8	74,5	21,6	2,1	0,26	2,985	2,48	0,27	0,82	6,414	2,12	0,90
186	6,3	1,3	73,0	24,2	1,5	0,31	3,016	2,46	0,30	0,92	6,444	2,11	0,94
196	8,4	0,5	78,0	20,0	1,5	0,36	3,006	2,46	0,35	1,31	6,442	2,11	1,35
204	11,2	0,4	83,0	15,3	1,3	0,37	2,958	2,50	0,40	1,86	6,500	2,09	1,69
207	11,9	0,5	81,0	18,5	—	0,44	3,013	2,46	0,43	1,93	6,481	2,10	1,82
215	15,0	0,3	83,0	16,7	—	0,50	3,009	2,46	0,49	2,49	6,466	2,10	2,40
215	14,5	—	—	—	—	0,48	2,991	2,47	0,49	2,41	6,457	2,10	2,40
220	15,2	0,5	82,5	16,2	0,8	0,52	2,996	2,47	0,52	2,51	6,440	2,11	2,79

TABLE 10. Dehydrogenation of Cyclohexene. MoS_2 ; volume 5 ml; $l = 2$ cm;
feed rate $A_1 = 70.6$; $\epsilon_{\text{H}_2} = 17.7$ kcal/mole; $k_0 = 1.39 \cdot 10^6$; $\frac{\epsilon_{\text{H}_2}}{\log k_0} = 2.89$; \underline{m} in
ml/min ml cat. NTP

Temper- ature, °C	m_{H_2}	$\lg k_0$	$\frac{\epsilon_{\text{H}_2}}{\lg k_0}$	m_{H_2} cal- culated with $\epsilon_{\text{H}_2} = 17.7$	Temper- ature, °C	m_{H_2}	$\lg k_0$	$\frac{\epsilon_{\text{H}_2}}{\lg k_0}$	m_{H_2} cal- culated with $\epsilon_{\text{H}_2} = 17.7$
400	0,24	6,136	2,89	0,24	446	0,57	6,443	2,88	0,55
420	0,35	6,133	2,89	0,35	446	0,55	6,428	2,89	0,55
429	0,36	6,075	2,91	0,41	473	0,89	6,439	2,89	0,87
433	0,48	6,165	2,87	0,44	483	0,97	6,111	2,90	1,01
440	0,49	6,124	2,89	0,49					

negligible splitting of the ring. Both catalysts rapidly lost their activity during dehydrogenation of hydrocarbons; MoS_2 lost it to a greater degree. The activation energy for cyclohexene on WS_2 No. 3 was equal to $\epsilon_{\text{H}_2} = 21$ kcal/mole, and on MoS_2 , $\epsilon_{\text{H}_2} = 17.7$ kcal/mole. By dehydrogenation of cyclohexane unsaturated substances were detected in the catalyst, which indicated an edgewise reaction mechanism. With regard to the conversion of isopropyl alcohol, WS_2 No. 3, WS_2 No. 1 and MoS_2 behaved differently: on WS_2 No. 3 and WS_2 No. 1 isopropyl alcohol underwent almost exclusively dehydration $\epsilon_{\text{H}_2\text{O}} = 17.4$ kcal/mole and $\epsilon_{\text{H}_2\text{O}} = 15.8$ kcal/mole respectively and on MoS_2 both dehydrogenation $\epsilon_{\text{H}_2} = 7.4$ kcal/mole and dehydration $\epsilon_{\text{H}_2\text{O}} = 13.6$ kcal/mole occurred.

The results obtained on tungsten sulfide and molybdenum sulfide permitted calculation of the bond energies of the atoms of the reacting molecules with the catalyst surface by means of the kinetic method proposed earlier [10, 11] Calculations were made by means of the formulae

$$\begin{aligned}
 Q_{\text{H-cat}} &= \frac{1}{3}(2\epsilon_3 - 2\epsilon_2 - \epsilon_1) + 62, \\
 Q_{\text{C-cat}} &= \frac{1}{3}(-2\epsilon_3 + 2\epsilon_2 - \epsilon_1) + 36,8, \\
 Q_{\text{O-cat}} &= \frac{1}{3}(-2\epsilon_3 - 2\epsilon_2 + 3\epsilon_1) + 48,7,
 \end{aligned}
 \tag{3}$$

where ϵ_1 , ϵ_2 , and ϵ_3 are the activation energies of the dehydrogenation of a hydrocarbon and an alcohol and dehydration of an alcohol respectively. In equations (3) the bond energies between atoms were taken from Kondrat'ev's results [12]; $Q_{C-H} = 98.7$; $Q_{C-O} = 85.5$; $Q_{O-H} = 110.8$ kcal/mole. For the industrial catalyst WS_2 No. 3, from the activation energies of dehydrogenation and dehydration of ethyl alcohol and dehydrogenation of cyclohexene we obtained $Q_{H-WS_2} = 57.2$; $Q_{C-WS_2} = 27.6$ and $Q_{O-WS_2} = 43.2$ kcal/mole. From the activation energies of dehydrogenation and dehydration of n-propyl alcohol and cyclohexane we obtained; $Q_{H-WS_2} = 58.0$; $Q_{C-WS_2} = 26.8$; $Q_{O-WS_2} = 54.2$ kcal/mole. For the MoS_2 catalyst, from the activation energies of dehydrogenation and dehydration of isopropyl alcohol and dehydrogenation of cyclohexene we obtained: $Q_{H-MoS_2} = 60.3$; $Q_{C-MoS_2} = 26.8$; $Q_{O-MoS_2} = 52.5$ kcal/mole. The relative adsorption coefficients of water and propylene on the WS_2 No. 3 and WS_2 No. 1 catalysts were not dependent on temperature or the difference in heats of adsorption $\Delta\lambda_{21} = 0$ and $\Delta\lambda_{31} = 0$ on both catalysts. Knowing the difference in the heats of adsorption of the reaction products and the true activation energy it was possible to calculate, by means of one of our proposed adsorption-kinetic methods [13], the bond energies from the formulae:

$$\begin{aligned} -\varepsilon_{H_2O} &= \frac{3}{4}(-Q_{C-H} - Q_{C-O} + 2Q_{C-WS_2} + Q_{H-WS_2} + Q_{O-WS_2}), \\ \Delta\lambda_{21} &= \alpha(Q_{C-H} + Q_{C-O} - Q_{C=C}) - \frac{3}{4}Q_{H-WS_2} - \frac{3}{4}Q_{O-WS_2}, \\ \Delta\lambda_{31} &= \alpha(Q_{C-H} + Q_{C-O} - Q_{O-H}) - \frac{3}{2}Q_{C-WS_2}. \end{aligned}$$

By combining all three equalities, we obtained an equation for calculating α , and knowing α it was possible to calculate Q_{C-WS_2} and $Q_{H-WS_2} + Q_{O-WS_2}$ from the last two equations. By this method in the case of dehydration of isopropyl alcohol on the industrial catalyst WS_2 No. 3 and on our prepared catalyst WS_2 No. 1 we obtained respectively: $Q_{C-WS_2} = 29.9$; $Q_{H-WS_2} + Q_{O-WS_2} = 98.3$ and $Q_{C-WS_2} = 30.2$; $Q_{O-WS_2} + Q_{H-WS_2} = 99.1$ kcal/mole. These values differ somewhat from the results obtained by the three reactions method, which is explained by the effect of the substitution of frames and in calculating by the three reactions method there are obtained not the true but the apparent activation energies.

While the location of Mo and W in one subgroup of Mendeleev's periodic system and the almost completely identical crystalline structures of WS_2 and MoS_2 points up the close catalytic properties of the WS_2 and MoS_2 catalysts, the difference in behavior of isopropyl alcohol on these catalysts indicates that the nature of the metal plays a part in the catalysis.

SUMMARY

1. It was shown that on the sulfide catalysts WS_2 and MoS_2 dehydrogenation and dehydration of alcohols and dehydrogenation of hydrocarbons take place, accompanied by partial cracking. The activation energies of these reactions were determined.
2. In respect to dehydrogenation of isopropyl alcohol MoS_2 was much more active than WS_2 ; in addition only dehydration took place on WS_2 , whereas dehydrogenation and dehydration occurred on MoS_2 .
3. The relative adsorption coefficients of the reaction products on the WS_2 catalysts were determined for the dehydration of isopropyl alcohol, revealing that the adsorption coefficients of propylene and water were the same on different samples of WS_2 and were not dependent on temperature.
4. The bond energies of the atoms C, H and O with the catalyst surface of WS_2 and MoS_2 were calculated by the three reactions kinetic method and by the adsorption-kinetic method.

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KINETICS AND MECHANISM OF THE REACTION OF THE CH_2OH RADICAL WITH O_2 MOLECULES

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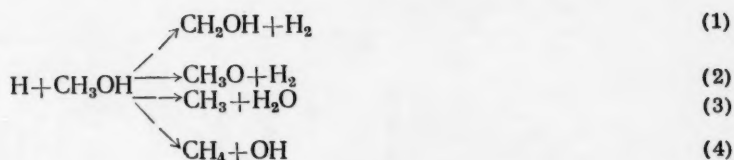
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Up until now the reaction of the alcohol radical CH_2OH has not been studied. Moreover there is no information in the literature on methods of preparing this radical. It has been found, as will be seen further on, that the CH_2OH radical is produced by the action of atomic hydrogen on a molecule of methyl alcohol.

At the outset it seemed possible that the reaction of a hydrogen atom with CH_3OH might take place by four paths:



Thus by reaction of a hydrogen atom with CH_3OH , the appearance of the four radicals CH_2OH , CH_3O , CH_3 and OH might be expected in principle. However by comparing reactions (1) and (2), it may be said at the outset that reaction (1) is the more probable since it follows from the results of a number of authors [1, 2] that the C-H bond is weaker than the O-H bond, and therefore the CH_2OH radical will be formed more readily than CH_3O . Reaction (4) can be disregarded in the present case since it does not result in formation of a radical containing carbon. Hydroxyl which might produce new active particles, was destroyed on the surface of the reaction vessel under our conditions, since the surface was coated with KCl. It was known that a KCl coated surface very actively destroys hydroxyl.

The work had two aims: 1) to discover whether there was mainly formation of some radical by the reaction ($\text{H} + \text{CH}_3\text{OH}$), and if there was, what it was precisely; 2) to study the kinetics and mechanism of the reaction of the resulting radical with oxygen.

EXPERIMENTAL

Experiments were carried out by means of the discharge tube method which we have described several times [3]. Atomic hydrogen was generated in the region of a high voltage discharge in dry hydrogen, and together with the non-dissociated molecules was passed through a jet into the reaction vessel. With the aim of achieving reproducibility of experiments - the walls of the reaction vessel and jet were coated with KCl. Methyl alcohol was fed to the jet in the reaction vessel at concentrations over an order greater than the concentration of atomic hydrogen. With such proportions of atomic hydrogen and alcohol the atomic hydrogen was consumed principally in the primary reaction with the alcohol. Molecular oxygen was introduced into the reaction vessel at a distance of 2.5 cm or more from the site of mixing of the methyl alcohol and atomic hydrogen. At such distances (with the conditions as described above) the concentration of atomic hydrogen fell to a value which we could not detect, for example, by means of a carbon black mirror, placed by the appropriate inlet into the stream. The reaction products were condensed in a detachable trap cooled with liquid nitrogen.

Prior to an experiment a known quantity of water was poured into the trap to dissolve the reaction products. After thawing, analysis of the products was carried out.

Among the possible stable reaction products of $H + CH_3OH$, without introduction of molecular oxygen, might be expected H_2 , CH_4 and H_2O , generated in the process (1)-(4), and $OHCH_2-CH_2OH$, CH_2O , CH_3OH , CH_3OOCH_3 , C_2H_6 being the products of recombination and disproportionation of the radicals. With introduction of molecular oxygen, among the reaction products might be expected, in addition to products originating without oxygen, formation of the appropriate peroxides. Analysis was not made for H_2 , CH_3OH and H_2O since these products were difficult to distinguish from the starting materials. Analysis was also not made for CH_4 since this gas was not condensed under the experimental conditions. Ethane and ethylene were determined by mass-spectrometric analysis of the gases condensed in the trap cooled with liquid nitrogen. Ethylene glycol was determined qualitatively, after distilling off methyl alcohol, by reaction with β -naphthol. Formaldehyde was analyzed by three methods: 1) polarographically; 2) by titration with hydroxylamine hydrochloride; 3) by reacting with a mixture of phenylhydrazine hydrochloride, potassium ferricyanide and HCl . After carrying out the reaction the solution was weakly alkaline (apparently due to ammonia, produced in the discharge owing to the presence of small amounts of nitrogen in the hydrogen). Titration with hydroxylamine hydrochloride was carried out after neutralizing the weakly alkaline solution. Peroxides were analyzed polarographically in HCl solution with prior removal of oxygen by blowing off with hydrogen, and also by titration with thiosulfate after running in an acid solution of KI .

Among the possible reaction products listed above, only formaldehyde, peroxides and ethane were detected in the experiment. Several series of experiments were carried out at different temperatures and pressures. The results of one series of experiments at 90° and 5.3 mm pressure are presented in Table 1.

TABLE 1. (Linear Flow Rate $w = 280$ cm/sec; Cross-sectional Area of the Vessel $s = 2.4$ cm²; Temperature 90°)

Pressure P total in mm Hg	O ₂ feed rate* 10 ⁻¹⁷ in mol. per sec through cm ²	Rate of formation			Pressure P total in mm Hg	O ₂ feed rate* 10 ⁻¹⁷ in mol. per sec through cm ²	Rate of formation		
		formal- dehyde* 10 ⁻¹⁶	perox- ides* 10 ⁻¹⁶	ethane* 10 ⁻¹⁶			formal- dehyde* 10 ⁻¹⁶	perox- ides* 10 ⁻¹⁶	ethane* 10 ⁻¹⁶
5,3	4,95	6,05	2,2	—	5,1	1,0	—	1,2	—
5,3	1,83	4,05	1,7	—	5,1	0,90	—	1,16	—
5,1	0	3,0	0	—	5,3	5,6	—	1,9	—
5,4	3,30	6,05	2,05	—	5,2	5,4	—	2,3	—
5,2	0	3,5	trace	—	5,2	5,8	—	2,3	—
5,5	5,30	8	1,83	—	5,2	5,85	—	2,4	—
5,3	0	4	trace	—	5,2	5,3	—	2,3	—
5,3	0	4	—	—	6,0	9,8	—	—	1,6
5,3	2,38	—	1,77	—	6,0	0	—	—	1,8
5,2	1,65	—	1,72	—	6,0	6,0	—	—	1,5
5,2	1,65	—	1,45	—	6,0	0	—	—	1,6
5,2	0,82	—	1,2	—					

*Rates of formation of the reaction products are expressed as number of molecules per second.

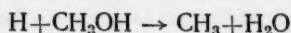
As seen from Table 1, in the experiments, carried out without introduction of molecular oxygen, both formaldehyde and ethane were detected in the reaction products. Quantitative determination of formaldehyde and ethane was not carried out at the same time. Peroxides (organic and hydrogen peroxide) were not detected or only found in trace amounts. Introduction of molecular oxygen into the stream lead to formation of hydrogen peroxides, an increase in the yield of formaldehyde, but did not affect the quantity of ethane formed.

Rather unexpectedly, formation of alkyl peroxide did not occur in these experiments when oxygen was introduced into the reaction zone, only hydrogen peroxide. The absence of alkyl peroxide formation under the experimental conditions and absence of effect of oxygen introduction on the yield of ethane leads to the conclusion that methyl radicals were not formed in the space of the reaction vessel. If methyl radicals were present in the reaction space, then on introduction of oxygen methyl hydroperoxide would be detected, and the yield of ethane would be decreased. The conclusion that methyl radicals are not present in the reaction space leads inevitably to the conclusion that the ethane detected experimentally was not formed in the reaction space.

Discussion of Experimental Results

A space process of ethane formation from methyl radicals and a depression of ethane formation by molecular oxygen were observed by Martin and Noyes [4]. Apparently under our experimental conditions, in the reaction of atomic hydrogen and alcohol a proportion of the atoms, as happens in the case of the reaction $\text{H} + \text{C}_2\text{H}_4$ [5], reacted on the surface of the vessel and ultimately resulted in formation of ethane. This surface reaction did not inhibit the course of the space reaction of atomic hydrogen and alcohol, and took place side by side with the space reaction.

Consequently reaction of atomic hydrogen and alcohol with formation of the $\text{CH}_3\cdot$ radical:

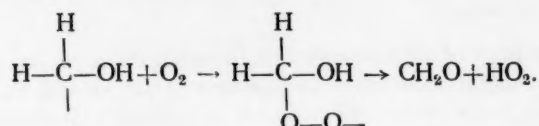


in the reaction space did not occur under our experimental conditions.

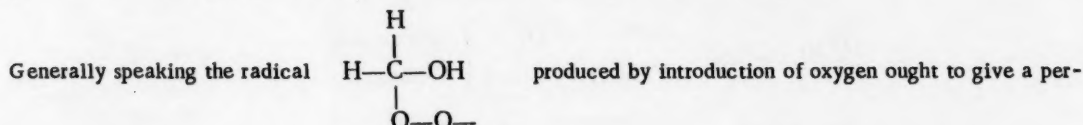
Consequently, of the three possible processes either (1) $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_2\text{OH}$ or (2) $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_3\text{O}$ took place.

At the beginning of the paper it was noted that process (1) is more probable than process (2).

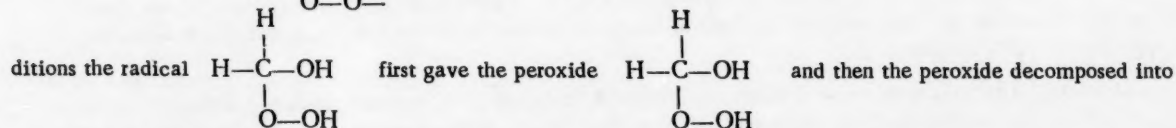
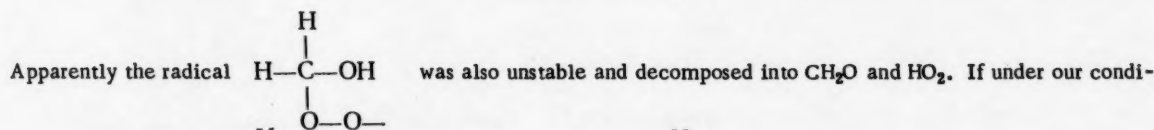
The reaction of CH_2OH and O_2 may be represented in the following way:



With the reaction products appeared formaldehyde, observed experimentally, and $\text{HO}_2\cdot$. The $\text{HO}_2\cdot$ radical was responsible for the formation of hydrogen peroxide. The quantity of formaldehyde approximately doubled on introducing oxygen (see Table 1). Such a two-fold increase indicated that, in the absence of oxygen, the radicals produced from the alcohol mainly disproportionated. If another process besides disproportionation occurred, then introduction of oxygen would lead not to double the quantity of formaldehyde but to a greater increase.

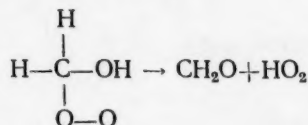


oxide. However a compound with two functional groups on one carbon atom would be produced. It is known that similar compounds (e.g., with two OH on one carbon, or with a halogen and OH) cannot exist and rapidly decomposes.



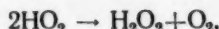
CH_2O and H_2O_2 , then peroxide and formaldehyde would be present in the same quantities. In our experiments this was not observed.

From Table 1 it is seen that the quantity of hydrogen peroxide found is approximately a third of that of the formaldehyde. Consequently the only theory which remains of the mechanism of formation of hydrogen peroxide agreeing with the experiment is decomposition of the radical.



and the subsequent process $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. The fact that not twice but three times less hydrogen peroxide than formaldehyde was formed can be explained by destruction of a proportion of the HO_2 radicals without formation of peroxide.

Formation of hydrogen peroxide from the HO_2 radical can occur not only by reaction of two HO_2

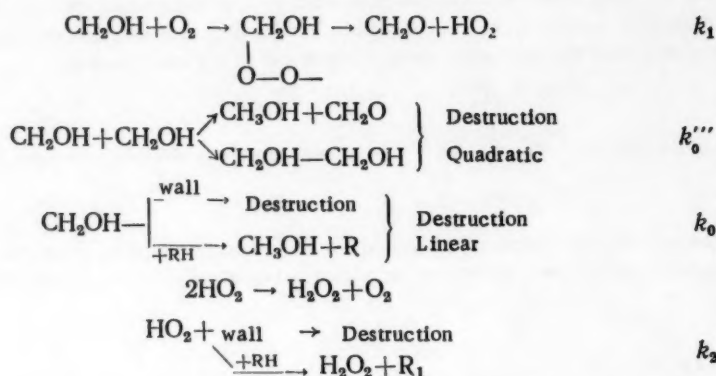


but also as a result of the reaction $\text{HO}_2 + \text{RH} \rightarrow \text{H}_2\text{O}_2 + \text{R}$, where RH is either H_2 or CH_3OH . Formation of hydrogen peroxide in this way does not conflict with the experimental fact that the quantity of hydrogen peroxide formed was three times less than the quantity of formaldehyde.

The problem of hydrogen peroxide formation from the HO_2 radical has an independent interest and we will return to it in another communication. We have shown that hydrogen peroxide is formed, mainly from HO_2 radicals, without participation of RH and that this process does not take place on the cold walls of the trap. Here it is essentially emphasized that from CH_2OH radical and O_2 , the HO_2 radical is formed, from which hydrogen peroxide results.

Thus the experimental results of a study of the reaction products from the reaction of atomic hydrogen with alcohol indicates that the principal primary reaction, under our conditions, in the reaction space was a reaction resulting in formation of the CH_2OH radical.

Measurement of the rate constants of the elementary reactions was the next most important problem having great bearing on knowledge of the total mechanisms of the reactions of radicals with molecules. The rate constant of the reaction of the CH_2OH radical with molecular oxygen was determined from the relationship between the final concentration of one of the reaction products — H_2O_2 , and the initial concentration of molecular oxygen. For measurement of the rate constant of the reaction of the CH_2OH radical with oxygen molecules by the known method [3] the following reaction scheme was adopted:



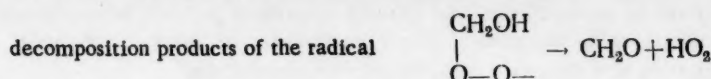
In this scheme k_1 is the rate constant of the reaction $\text{CH}_2\text{OH} + \text{O}_2$; k_0 is the total rate constant of the linear destruction of radicals; k_0''' the total rate constant of quadratic destruction of radicals; k_2 is the rate constant of disappearance of HO_2 radicals.

Since a CH_2OH radical reacts with molecular oxygen by only one path, and as a result of the reaction produces CH_2O and HO_2 , then according to our method [3] of measuring the constants the reciprocal of the final concentration of the primary product of the initial concentration of oxygen is expressed in the following form:

$$\frac{1}{(\text{B})_k} = \frac{1}{R_0} + \frac{k_0 + k_0''' (R_0)}{k_1 (\text{O}_2)_0 (R)_0}, \quad (5)$$

where $(\text{B})_k$ is the final concentration of the unstable product $\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{O}-\text{O}- \end{array}$ disregarding decomposition and destruction; R_0 is the initial concentration of $-\text{CH}_2\text{OH}$

Since direct measurements of the concentration $(B)_K'$ were impossible owing to the lack of a suitable method, it was necessary to find another way which gave a reliable result. We chose the alternative way of measuring the



According to the scheme for the reaction mechanism it is possible to write the equality

$$(B)_F' = (\text{CH}_2\text{O})_F = (\text{HO}_2)_F' \quad (6)$$

where (CH_2O) is the final concentration of formaldehyde, formed via the radical $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{O}-\text{O}- \end{array}$; $(\text{HO}_2)_F'$ is the final concentration of the HO_2 radical disregarding its destruction.

Use of the final concentration of formaldehyde can lead to an incorrect value for the rate constant of the reaction of CH_2OH with O_2 , since formaldehyde is not only a reaction product of $\text{CH}_2\text{OH} + \text{O}_2$, but also results from disproportionation of CH_2OH . Determinations of the constant in our experiments were made from the yield of hydrogen peroxide. The quantity $(\text{HO}_2)_F'$ can be replaced in Eq. (6) by the concentration of peroxide.

The $(\text{HO}_2)_F'$ radical concentration can be represented as the total quantity proportional to the peroxide concentration, and the concentration of (HO_2) perishing:

$$(\text{HO}_2)_F' = (\text{HO}_2)_{\text{dest}} + b (\text{H}_2\text{O}_2)_F.$$

The concentration of $(\text{HO}_2)_{\text{dest}}$ perishing can be expressed by the concentration $(\text{HO}_2)_F'$, since the concentration which is disappearing is proportional to the original concentration.

Therefore

$$(\text{HO}_2)_F' = a (\text{HO}_2)_F' + b (\text{H}_2\text{O}_2)_F,$$

for which

$$(\text{HO}_2)_F' = \frac{b (\text{H}_2\text{O}_2)_F}{1-a} = k (\text{H}_2\text{O}_2)_F. \quad (7)$$

Then using Eqs. (5) and (6) we get the relationship of the initial concentration of peroxide to $(\text{O}_2)_0$, expressed by the following equation:

$$\frac{1}{(\text{H}_2\text{O}_2)_F} = \frac{k}{(R)_0} + \frac{[k_0 + k_0''' (R)_0] k}{k_1 (\text{O}_2)_0 (R)_0}. \quad (8)$$

Equation (8) [as well as Eq. (5)] is the equation of a straight line. The value $k/(R)_0 = b$ is the intercept of the ordinate. This value of the intercept is inversely proportional to the initial concentration of the CH_2OH radicals.

The quantity $-\frac{k_0 + k_0''' (R)_0}{k_1} \cdot \frac{k}{(R)_0} = \tan \alpha$ is the tangent of the angle of slope of the straight line. From which the sought value of the reaction rate constant k_1 can be written in the form:

$$k_1 = \frac{[k_0 + k_0''' (R)_0] \cdot b}{\tan \alpha}. \quad (9)$$

Thus by plotting the relationship $1/(\text{H}_2\text{O}_2)_F$ against $1/(\text{O}_2)_0$, from the intercept on the ordinate and the tangent of the angles of slope, with the condition that the sum of the destroyed radicals $k_0 + k_0''' (R)_0$ is known, we find the value of k_1 .

The total quantity of CH_2OH radical destroyed under our experimental conditions was also measured. We have described the method for determining the destruction constant of radicals earlier [6]. In order to determine the total

destruction of radicals it is at least necessary to measure the relative concentration of radicals according to the length of the reaction vessel. The relative concentration of CH_2OH radicals at different points of the reaction vessel was determined from the relative limiting yields of peroxide, since the limiting quantity of peroxide is proportional to the radical concentration. In addition the ratio R_0/R_x was plotted against the distance x , where R_0 is the initial concentration, and R_x is the radical concentration at a distance x from the original concentration.

In a previous paper it was shown [6] that if the relationship between $(R_0/R)_x$ and x is obtained as a straight line, not passing through the origin of the coordinates, then in this case a quadratic destruction predominates, which can be written as the inequality

$$k_0 \ll k_0''' (R)_0.$$

In Fig. 1 is presented the relationship between $(R_0/R)_x$ and x for a temperature of 110° and pressure of 5.3 mm. The straight line by not passing through the origin of the coordinates, indicates that a quadratic destruction of the CH_2OH radicals predominates. This agrees with the conclusion made above that the CH_2OH radicals mainly disproportionate. Values of the destruction constants are calculated from these straight line plots by the formula

$$k_0''' (R)_0 = w \tan \gamma,$$

where w is the linear flow rate and $\tan \gamma$ is the tangent of the angle of slope of the line. As seen from Fig. 1, in the present work, molecular oxygen was introduced at a distance of 2.5, 6.5 and 9.5 cm, from the zero point. But the zero point was at a distance of 2.5 cm from the point of mixing of the atomic hydrogen and alcohol. The value of the quantity $k_0''' (R)_0$ calculated from the straight line plot of Fig. 1 equalled 53 sec^{-1} .

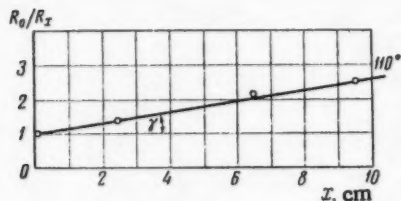


Fig. 1. Relationship between the relative concentration of the CH_2OH radical and distance at 110° and $p_{\text{total}} = 5.3 \text{ mm}$.

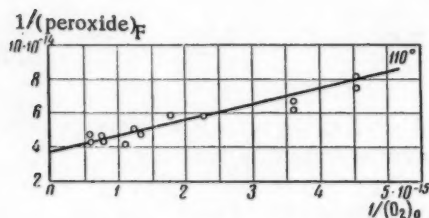
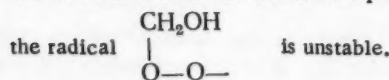


Fig. 2. Relationship between the reciprocal of the final hydrogen peroxide concentration and the reciprocal of the initial molecular oxygen concentration for reaction of the CH_2OH radical with molecular oxygen at 110° and $p_{\text{total}} = 5.3 \text{ mm}$ of Hg.

that the reaction occurs without the participation of third particles. In the present case this once again indicates that



In Fig. 2 is presented the relationship between the reciprocals of the final peroxide concentrations and $1/(\text{O}_2)_0$. From the intercept on the ordinate the tangent of the angle of slope and the values of the amount destroyed $k_0''' (R)_0$, the value $k_1 = 1.98 \cdot 10^{-13} \text{ cm}^3 \cdot \text{sec}^{-1}$ was obtained by means of formula (5). In an analogous way measurement of the quantities $k_0''' (R)_0$ and k_1 at different temperatures and pressures was carried out. In Table 2 are given the values of these quantities. In Fig. 3 is shown the Arrhenius dependence of k_1 . The activation energy calculated from the graph equalled $E = 2500 \pm 500 \text{ cal}$. Thus it is possible to write the expression for the rate constant as

$$k_1 = 1.95 \cdot 10^{-13} \sqrt{T} \cdot e^{-\frac{2500}{RT}} \text{ cm}^3 \cdot \text{sec}^{-1}.$$

Values of the constant obtained for different pressures in the range 2.5-12 mm, show (see Table 2) that the rate constant

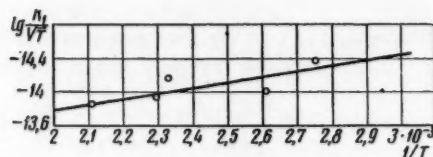


Fig. 3. Temperature dependence of the effective rate constant of the reaction of the CH_2OH radical with molecular oxygen, $E = 2500 \text{ cal}$.

of the reaction of the CH_2OH radical with oxygen did not depend on the pressure. The absence of pressure dependence indicates

TABLE 2

Pressure mm of mercury	Temper- ature, °K	Flow rate w cm/sec	Total des- truction $k_0 \cdot 10^3 (R_0)$	Reaction rate constant $k_1 \cdot 10^{13}$
5,2	363	280	42	0,84
5,2	383	332	53	1,98
5,2	428	340	64	1,28
5,2	436	354	67	2,57
5,2	473	393	98	3
2,5	428	260	28,6	0,9
12	428	470	84,5	0,85

SUMMARY

1. By reaction of atomic hydrogen with molecular methyl alcohol the radical CH_2OH is formed.
2. Reaction of the CH_2OH radical with molecular oxygen results in formation of the unstable complex $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{O}-\text{O} \end{array}$, which decomposes into formaldehyde and the HO_2 radical.
3. The absolute values of the rate constant and activation energy of the reaction of the alcohol radical CH_2OH with molecular O_2 were measured.
4. The rate constant of the reaction of CH_2OH radical with O_2 did not depend on pressure.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

RATE CONSTANT AND MECHANISM OF THE REACTION OF ATOMIC OXYGEN WITH METHYL ALCOHOL

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

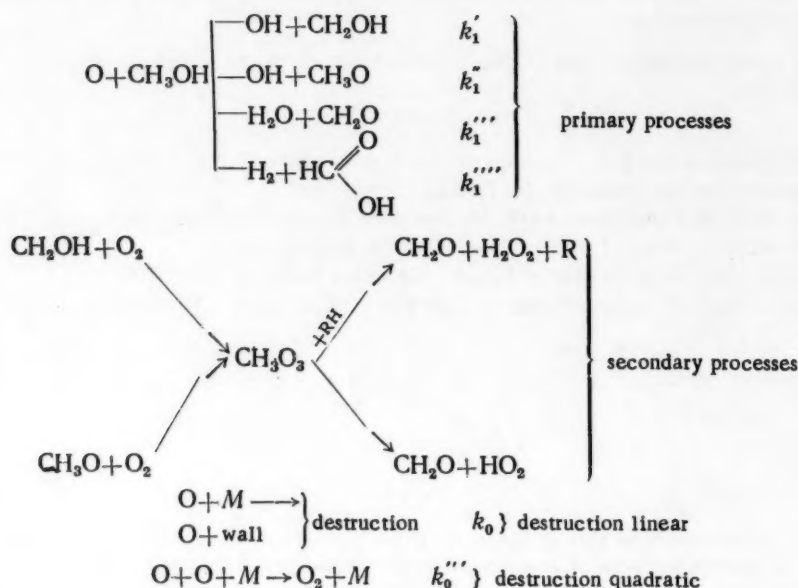
No. 4, pp. 599-603, April, 1961

Original article submitted February 26, 1960

The present work is one of a planned series of investigations aimed at studying the general mechanisms of reactions of atoms and radicals.

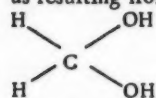
There are very few publications relating to investigations of reactions of atoms and radicals. Observations of reactions in flames [1-4] and investigations of the spectra of these flames [3-4] have been published.

Starting from general considerations, the products produced according to the following scheme can be expected as the primary and secondary reaction products.



M is the concentration of third particles.

In this scheme the different types of exothermic reactions of atomic oxygen are taken into consideration and endothermic primary processes omitted. The formation of formaldehyde in the primary process k_1''' can be considered as resulting from addition of an oxygen atom across the C-H bond with formation of the unstable molecule



which, in accordance with the known property of an organic molecule having two hydroxyl groups

on one carbon atom, must be unstable and decompose into water and formaldehyde. This process can also be considered

as resulting from the elimination of two hydrogen atoms with formation of water and the diradical $\begin{array}{c} \diagup \quad \text{H} \\ \text{C} \\ \diagdown \quad \text{OH} \end{array}$, which isomerizes to formaldehyde. Formation of formaldehyde and hydrogen peroxide in the secondary reaction will occur either as a result of decomposition of the unstable compound $\begin{array}{c} \text{H} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OOH} \end{array}$ (into CH_2O and H_2O_2), in which one carbon atom has a hydroxyl and a peroxide group, or as a result of decomposition of the peroxide radical $\begin{array}{c} \text{H} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OO} \end{array}$ (into CH_2O and HO_2) if the radical is unstable. The HO_2 radical leads to formation of hydrogen peroxide.

EXPERIMENTAL

Experiments were carried out in the jet vacuum apparatus of the type described earlier [5, 6]. In the experiments conditions were maintained under which a flame was not observed, and when both the primary products of the reaction of atomic oxygen and methanol, and the secondary products — products of the reaction of the primary radicals, with molecular oxygen were formed they were collected. Atomic oxygen was generated by means of a high voltage discharge in a stream of molecular oxygen. To avoid nitrogen and water vapor impurities, molecular oxygen was prepared by heating chemically pure potassium permanganate, previously evacuated to 10^{-3} mm·Hg. Before admitting the oxygen into the discharge it was carefully dried by a system of traps, cooled with liquid nitrogen. In order to ensure reproducibility in the experiments the reaction vessel was coated with potassium chloride. The generating zone of the atomic oxygen was separated from the reaction zone by the jet-nozzle.

Formaldehyde was determined by titration with hydroxylamine hydrochloride and also by a polarographic method. Peroxide were analyzed polarographically in HCl solution with prior expulsion of oxygen with hydrogen, peroxides were also determined by titration with thiosulfate after adding an acid solution of KI.

Our search of the various oxygen containing reaction products in the trap, cooled with liquid nitrogen, led to one main product — formaldehyde. Besides formaldehyde, H_2O_2 was detected. The quantity of H_2O_2 was found to be less by an order of magnitude than the quantity of formaldehyde. Acid was not detected even in trace amounts.

The rate constant of the reaction of atomic oxygen with methyl alcohol can be determined by a method [5], recently published. In accordance with this method the total rate constant of all the primary processes k_1 representing the sum $k_1 = k_1' + k_1'' + k_1''' + k_1''''$ was determined from the rate of accumulation of one of the primary reaction products. In particular, since in the present case formaldehyde was the principal product, on the basis of the proposed method and the adopted general scheme of the reaction mechanism, the absolute value k_1 for the reaction $\text{O} + \text{CH}_3\text{OH}$ was determined from the equation:

$$\frac{1}{(\text{CH}_2\text{O})_F} = \frac{k_1}{k_1'''(\text{O})_0} + \frac{[k_0 + k_0'''(M)(\text{O})_0]k_1}{k_1k_1'''(\text{O})_0} \cdot \frac{1}{(\text{CH}_3\text{OH})_0}, \quad (1)$$

where $(\text{CH}_2\text{O})_F$ is the final concentration of formaldehyde; $(\text{O})_0$ is the initial concentration of atomic oxygen; $(\text{CH}_3\text{OH})_0$ is the initial concentration of methanol; (M) is the concentration of oxygen molecules; k_0 , k_0''' , k_1 and k_1''' are the rate constants of the corresponding elementary reactions (see scheme).

Equation (1) represents a straight line with coordinates $\frac{1}{(\text{CH}_2\text{O})_F}$ and $\frac{1}{(\text{CH}_3\text{OH})_0}$. The quantity $k_1/k_1'''(\text{O})_0 = c$ is the intercept on the ordinate. In order to determine the absolute value from the tangent of the angle of slope of the straight line, corresponding to Eq. (1), in addition to the relationship between $\frac{1}{(\text{CH}_2\text{O})_F}$ and $\frac{1}{(\text{CH}_3\text{OH})_0}$, it is necessary to know the sum $[k_0 + k_0'''(M)(\text{O})_0]$. This sum was determined by measurements of the relative concentrations of atomic oxygen at different points of the reaction vessel. The details of the method for determining the sum $[k_0 + k_0'''(M)(\text{O})_0]$ was described in reference [7].

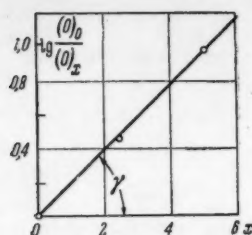


Fig. 1. Relationship between the relative concentration of atomic oxygen and the distance from the point of mixing of the atoms with methyl alcohol.

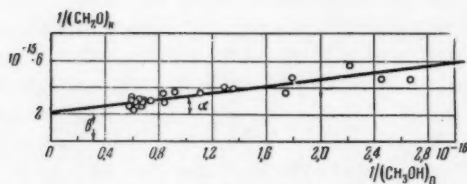


Fig. 2. Relationship of the final formaldehyde concentration and the initial methyl alcohol concentration.

In Fig. 1 are presented the results of measuring the relative concentrations of oxygen at different points of the reaction vessel at a temperature of 122° and pressure $p_{O_2} = 5.2$ mm Hg. From Fig. 1 it is seen that the relationship between $\lg (O)_0/(O)_x$ and x is a straight line. The straight line relationship between $\lg (O)_0/(O)_x$ and x indicates that the destruction of atomic oxygen is predominantly linear [7]. It must be noted that we have observed only linear destruction for atomic oxygen. For the case of linear destruction the destruction constant of atomic oxygen was determined from the tangent of the angle of slope of the straight line represented in Fig. 1. The destruction constant is

$$k_0 = 2,3w \operatorname{tg} \gamma, \quad (2)$$

where w is the linear flow rate.

In Fig. 2 is presented the relationship between $\frac{1}{(CH_2O)_x}$ and $\frac{1}{(CH_3OH)_0}$ for a temperature of 122° and pressure of 5.2 mm Hg. From the value of the intercept on the ordinate and the tangent of the angle of slope we obtain the value k_1 — the rate constant of the reaction of atomic oxygen with alcohol:

$$k_1 = \frac{k_0 \cdot b}{\operatorname{tg} \alpha} \quad (3)$$

In an exactly similar way measurements of the constants k_0 and k_1 were carried out at other temperatures and pressures. The results of these measurements are presented in the table.

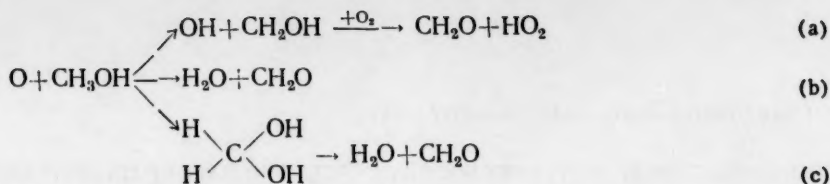
Temperature, °K (p mm Hg)	$k_0 \text{ sec}^{-1}$	$k_1 \cdot 10^{14} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{mole}^{-1}$	Temp. °K (p mm Hg)	$k_0 \text{ sec}^{-1}$	$k_1 \cdot 10^{14} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{mole}^{-1}$
347 (4,1)	50	0,9	423 (4,1)	80,0	2,65
353 (5,2)	62,5	1,0	483 (5,2)	153,0	2,9
363 (4,1)	65,0	1,18	506 (4,1)	160,0	4,55
389 (4,1)	70,0	1,75	363 (2,0)	65,0	1,05
395 (5,2)	97,0	1,85	393 (2,0)	40,5	1,4
399 (4,0)	75,0	1,2	363 (14,0)	85,0	0,7

As seen from the table, in the pressure range in which the measurements were made (2-14 mm) the existence of a dependence of the rate constant k_1 on the pressure at the same temperature was not observed. From this fact it may be concluded that the measured rate constant is of a constant bimolecular process and that consequently a third particle does not play any appreciable part in the reaction of atomic oxygen with molecular alcohol. In Fig. 3 the values of $\lg k_1$ are plotted against $1/T$ for pressures of 4 and 5 mm Hg. The activation energy obtained from Fig. 3 equals 3100 ± 500 cal.

Thus for the rate constant of the reaction $O + CH_3OH$ the following expression is obtained:

$$k_1 = 0,85 \cdot 10^{-12} e^{-\frac{3100}{RT}} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{mole}^{-1} \quad (4)$$

Since under the experimental conditions practically the sole product of the reaction is formaldehyde, then the constant obtained represents in fact the rate constant of formaldehyde formation. Formation of formaldehyde by the reaction $O + CH_3OH$ is conceivable by three paths



Formation of formaldehyde by path (a) is inconsistent with the experimental results we obtained. By this path together with formaldehyde, HO_2 is obtained, which leads to peroxide formation. We have carried out experiments [8] to study the reaction of the CH_2OH radical with O_2 under conditions comparable with the experimental conditions of the present investigation. The CH_2OH was obtained by the action of atomic hydrogen on methyl alcohol. We found that a hydrogen atom reacts with alcohol only with elimination of a H atom. The radical obtained with oxygen in fact results in formation of formaldehyde. But in this way hydrogen peroxide is also produced in quantities comparable with the quantity of CH_2O . Under the conditions of the reaction $\text{O} + \text{CH}_3\text{OH}$ hydrogen peroxide is produced to an order of magnitude less than CH_2O which indicates the small part played by process (a). Thus during interaction of O with CH_3OH the principal reactions are (b) or (c).

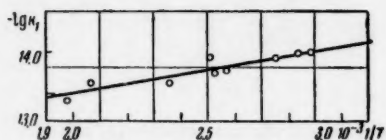


Fig. 3. Temperature dependence of the rate constant of the reaction of atomic oxygen with methyl alcohol.

Under our experimental conditions we will be unable to differentiate which of the two processes (b) or (c) predominates. However, judging by other examples of the reaction of atomic O, we conclude that process (c) takes place, proceeding by an initial addition of an O atom across the C-H bond. Since however, in addition to formaldehyde, hydrogen peroxide is detected, even though in considerably smaller quantities it may be concluded that process (a) also occurs under our experimental conditions but with considerably less probability. With regard to the remaining processes in the scheme, namely the process with constant k_1^{III} , then under our experimental conditions it proceeds at a negligibly small rate.

SUMMARY

1. The mechanism of the reaction of atomic oxygen with methyl alcohol in a jet has been studied. The principal carbon containing reaction product was formaldehyde, formed in the initial act of the interaction of atomic oxygen with alcohol.
2. The absolute values of the rate constant of the reaction of atomic oxygen with methyl alcohol at temperatures in the region 347-506°K and pressures 2 to 14 mm, were measured. The energy of activation of the reaction was determined.
3. Reaction of atomic oxygen with methyl alcohol proceeds by a bimolecular mechanism without participation of third particles.

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PHOSPHORUS-ORGANIC MONOESTERS

COMMUNICATION 3. VINYLTHIOPHOSPHINIC ACID AND SOME OF ITS DERIVATIVES

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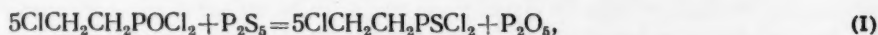
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In the first two communications of this series [1, 2] we described the dichloro anhydrides and several other derivatives of vinylphosphinic, α -chloro- and α -bromovinylphosphinic acids. In the present article we are presenting the synthesis of the dichloro anhydride and several derivatives of vinylthiophosphinic acid.

By the interaction of dichloro anhydride of β -chloroethylphosphonic acid with phosphorus pentasulfide according to the reaction discovered by Kabachnik and Godovikov [3], there was obtained the dichloro anhydride of β -chloroethylthiophosphinic acid (I),

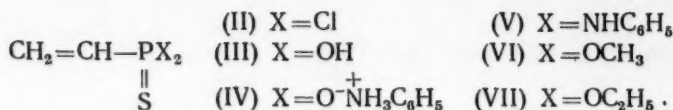


and from the latter by reaction with triethylamine in ether solution there was synthesized the dichloro anhydride of vinylthiophosphinic acid (II),

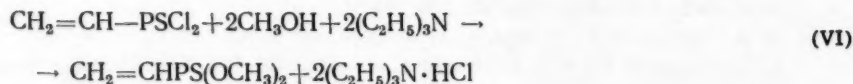


The dichloro anhydride of vinylthiophosphinic acid could be obtained also by the action of phosphorus pentasulfide on the dichloro anhydride of vinylphosphinic acid, however the yield in this case was small, probably because of polymerization caused by the long heating.

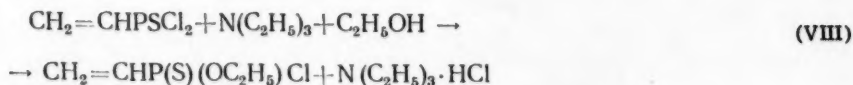
The dichloro anhydride of vinylthiophosphinic acid on hydrolysis is transformed into free vinylthiophosphinic acid (III), which was obtained as a syrup; the aniline salt of the acid (IV) melts with decomposition of 105-106°. By the interaction of the dichloro anhydride with aniline there was obtained the dianilide of vinylthiophosphinic acid (V)



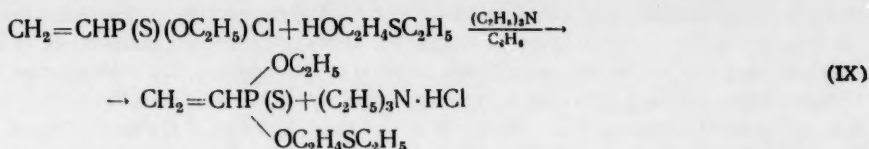
By the reaction of the dichloro anhydride of vinylthiophosphinic acid with 2 moles of methyl alcohol in the presence of 2 moles of base there was obtained its dimethyl ester (VI)



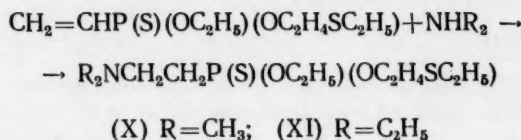
The diethyl ester of vinylthiophosphinic acid (VII) was also synthesized by the interaction of the dichloro anhydride of this acid with sodium ethylate. By using only one mole of alcohol and one mole of base one can obtain the ester chloro anhydride (VIII)



The latter, on reaction with a second molecule of alcohol forms the full ester. In this way there were obtained mixed esters, for example, the ethyl- β -ethylmercaptoethyl ester of vinylthionphosphinic acid (IX).

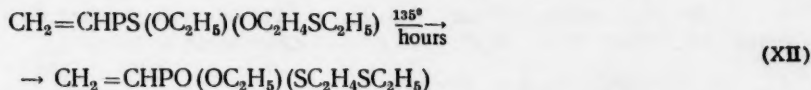


Using as an example the substance (IX), we investigated several addition reactions of the double bond in compounds of this type. It turned out that they easily add secondary amines with the formation, as we think, of β -substituted derivatives, for example



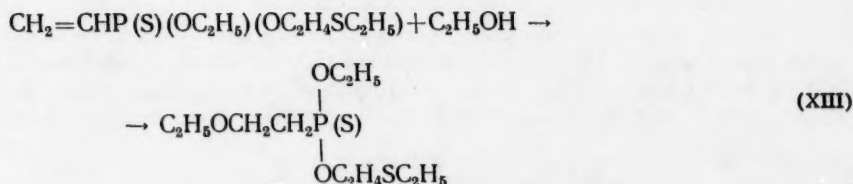
In this way were obtained the ethyl- β -ethylmercaptoethyl esters of β -dimethylaminoethylthionphosphinic acid (X) and β -diethylaminoethylthionphosphinic acid (XI).

A thion-thiol isomerization of the ethyl- β -ethylmercaptoethyl ester of vinylthionphosphinic acid was realized.



In this way there was obtained the O-ethyl-S- β -ethylmercaptoethyl ester of vinylthiophosphinic acid (XII).

It was also found that the ethyl- β -ethylmercaptoethyl ester of vinylthionphosphinic acid and also the product of its isomerization could add a molecule of alcohol to the double bond. The reaction proceeded when the unsaturated ester was heated with alcohol in the presence of sodium methylate



There were formed the corresponding esters of ethoxyethylthionphosphinic acid (XIII) and ethoxyethylthiolphosphinic (XIV). It can be assumed that the ethoxyl group under these conditions enters into the beta position.

EXPERIMENTAL DATA

The dichloro anhydride of β -chloroethylthiophosphinic acid (I).

To 181.5 g (1 M) of the dichloro anhydride of β -chloroethylphosphinic acid was added 80.5 g (0.36 M) of phosphorus pentasulfide, and the mixture was heated with stirring in a current of carbon dioxide at 155-160° for 6 hours. The liquid which was driven off from the reaction mixture in the stream of carbon dioxide was washed with ice water and its ether solution was dried over sodium sulfate. After distilling off the ether, the residue was distilled in vacuo; a substance was obtained with b.p. 85-86° (9 mm); 92 g (47%); n_D^{20} 1.5665; d_4^{20} 1.5117; found MR 42.64; calculated MR 42.67. It was a mobile liquid with a sharp unpleasant odor. Found: C 12.4; 12.0; H 1.8; 2.0; P 15.7; 15.1%. $\text{C}_2\text{H}_4\text{PSCl}_2$. Calculated: C 12.2; H 2.1; P 15.7%.

The dichloro anhydride of vinylthiophosphinic acid (II).

To 118 g (0.6 M) of the dichloro anhydride of β -chloroethylthiophosphinic acid in 350 ml of ether, 60.5 g (0.6 M) of triethylamine was added gradually with stirring and cooling (0-4°). After the addition of the triethylamine the reaction mixture was stirred for 30 min. at 0°; afterward, it was gradually raised to room temperature, and for one hour was heated at the boiling point. After removal of the sediment, the ether solution was washed with a 1% solution of hydrochloric acid and afterward with water. After drying over sodium sulfate, the ether was removed and the residue was distilled in vacuo. A substance was isolated with b.p. 54-55° (12 mm); 66 g (68%); n_D^{20} 1.5623; d_4^{20} 1.3954; found MR 37.43; calculated MR 37.34. Found: C 14.8; 14.8; H 1.9; 1.9; P 19.4; 19.2; Cl 43.6; 43.7%. $C_2H_3PSCl_2$. Calculated: C 14.9; H 1.9; P 19.2; Cl 44.0%.

The dichloro anhydride (II) which was obtained from 14.5 g (0.1 M) of the dichloro anhydride of vinylphosphinic acid and 8.05 g (0.036 M) of phosphorus pentasulfide had a b.p. of 52-55° (9 mm); 5.4 g (33%); n_D^{20} 1.5610; d_4^{20} 1.3956; found MR 37.37; calculated MR 37.34.

Vinylthiophosphinic acid (III).

A mixture of 4.83 g (0.03 M) of the dichloro anhydride of vinylthiophosphinic acid and 25 ml of water was allowed to stand at room temperature until the lower layer disappeared. After the water and the hydrochloric acid were distilled off, the substance was dried in vacuo over phosphorus pentoxide and alkali at 60° to constant weight. A viscous substance was obtained 3.2 g (86%). Found: C 19.0; 18.8; H 4.5; 4.4; P 24.2; 24.1%. $C_2H_3PSO_2$. Calculated: C 19.3; H 4.1; P 24.9%. The substance was strongly hygroscopic.

The aniline salt of vinylthiophosphinic acid (IV).

To 2.48 g (0.02 M) of vinylthiophosphinic acid was added 1.86 g (0.02 M) of aniline; the precipitate was washed with ether and recrystallized from alcohol. The substance obtained, 2 g (46%), melted with decomposition at 105-106°. Found: N 6.6; 6.7%. $C_8H_{12}PSO_2N$. Calculated: N 6.5%.

The dianilide of vinylthiophosphinic acid (V).

A mixture of 2 g (0.012 M) of the dichloro anhydride of vinylthiophosphinic acid and 4.6 g (0.05 M) of aniline in 10 ml of benzene was heated for 30 min. over a boiling water bath. The precipitate was separated, washed with water to remove aniline hydrochloride, and recrystallized from alcohol. The yield was 1.8 g (53%), m.p. 112-113°. Found: C 61.1; 61.0; H 5.5; 5.5; P 11.0; 11.0; S 11.6; 11.8; N 10.2; 10.3%. $C_{14}H_{18}OSN_2$. Calculated: C 61.3; H 5.5; P 11.3; S 11.7; N 10.2%.

The dimethyl ester of vinylthiophosphinic acid (VI).

This was obtained by the regular procedure from 12.1 g (0.075 M) of the dichloro anhydride of vinylthiophosphinic acid, 4.65 g (0.15 M) of methyl alcohol and 15.12 g (0.15 M) of triethylamine in 70 ml of ether; the yield was 7 g (61.5%), b.p. 82-83° (20 mm); n_D^{20} 1.4912; d_4^{20} 1.1382; found: MR 38.79; calculated MR 38.56. Found: C 31.4; 31.6; H 5.8; 6.0; P 20.2; 20.1%. $C_4H_8PSO_2$. Calculated: C 31.6; H 6.0; P 20.4%.

The diethyl ester of vinylthiophosphinic acid (VII).

This was obtained from 6.9 g (0.1 M) of sodium ethylate and 8.2 g (0.05 M) of the dichloro anhydride of vinylthiophosphinic acid in benzene; b.p. 75-76° (10 mm); yield 3.6 g (40%); n_D^{20} 1.4788; d_4^{20} 1.0589; found MR 48.24; calculated MR 47.79. Found: C 40.0; 40.1; H 7.1; 7.2; P 17.1; 17.0%. $C_6H_{12}PSO_2$. Calculated: C 40.0; H 7.3; P 17.2%.

The ester chloro anhydride of vinylthiophosphinic acid (VIII).

To 64.4 g (0.4 M) of the dichloro anhydride of vinylthiophosphinic acid in 350 ml of ether at 0-6° was slowly added with mixing a mixture of 40.4 g (0.4 M) of triethylamine and 18.4 g (0.4 M) of absolute ethyl alcohol. Afterward the temperature in the flask was gradually raised to room temperature and the mixture was boiled for 1 hour. After removal of the precipitate and the ether, the residue was distilled in vacuo. A substance was isolated with b.p. 71-73° (12 mm); 59 g (87%); n_D^{20} 1.5117; d_4^{20} 1.2019; found MR 42.57; calculated MR 42.98. Found: C 27.9; 28.0; H 4.7; 4.8; P 18.3; 18.6; Cl 20.7; 20.7%. C_4H_8PSClO . Calculated: C 28.2; H 4.7; P 18.2; Cl 20.8%.

The O-ethyl-O- β -ethylmercaptoethyl ester of vinylthiophosphinic acid (IX).

To 5.3 g (0.05 M) of β -hydroxyethyl sulfide and 2.0 g (0.05 M) of finely divided caustic soda in 30 ml of benzene was slowly added 8.5 g (0.05 M) of the ester chloro anhydride of vinylthiophosphinic acid (VIII) at 10° during

40 min. Afterward the reaction mixture was heated for 1 hr. at 60-70°. After removal of the precipitate, the filtrate was washed with cold water and dried over sodium sulfate; after removal of the benzene, the residue was distilled in vacuo. A substance was isolated with b.p. 135-136° (4 mm); 74.5-75° (5 · 10⁻⁵ mm) 6 g (50%); n²⁰_D 1.5139; d²⁰₄ 1.1088. Found MR 65.25; calculated MR 65.10. Found %: C 40.2; 40.0; H 7.1; 7.0; P 13.0; 13.0. C₈H₁₇PO₂S₂. Calculated %: C 40.0; H 7.1; P 12.9.

The O-ethyl-O-β-ethylmercaptoethyl ester of N-dimethylaminoethylthiophosphinic acid (X).

To 3.5 g (0.015 M) of the O-ethyl-O-β-ethylmercaptoethyl ester of vinylthiophosphinic acid was added with mixing 2.4 g (0.053 M) of dimethylamine. Afterward the reaction mixture was heated (reflux condenser with solid carbon dioxide). A substance was isolated by vacuum distillation with b.p. 80-82° (6 · 10⁻⁵ mm); 3.3 g (79%); n²⁰_D 1.5039; d²⁰₄ 1.0669; Found MR 79.20; calculated MR 79.78. Found: C 42.5; 42.3; H 8.7; 8.5; P 10.8; 10.7; S 22.1; 22.1; N 5.3; 5.2%. C₁₀H₂₄PNS₂O₂. Calculated: C 42.1; H 8.5; P 10.8; S 22.5; N 4.9%.

The O-ethyl-O-β-ethylmercaptoethyl ester of N-diethylaminoethylthiophosphinic acid (XI).

This was obtained from 4.8 g (0.02 M) of the O-ethyl-O-β-ethylmercaptoethyl ester of vinylthiophosphinic acid and 2.4 g (0.033 M) of diethylamine in a fashion similar to the last preparation: b.p. 89-91° (2 · 10⁻⁴ mm); 4 g (64%); n²⁰_D 1.5004; d²⁰₄ 1.0488; found MR 87.96; calculated MR 87.98. Found: C 45.6; 45.9; H 8.8; 8.9; P 9.8; 9.9; S 20.7; 20.6; N 4.6; 4.7%. C₁₂H₂₈PS₂NO₂. Calculated: C 46.0; H 9.0; P 9.9; S 20.5; N 4.5%.

The O-ethyl-S-β-ethylmercaptoethyl ester of vinylthiophosphinic acid (XII).

Five grams of the O-ethyl-O-β-ethylmercaptoethyl ester of vinylthiophosphinic acid (IX) was heated for 8 hours at 135°. The product was distilled in vacuo: b.p. 84-85° (2 · 10⁻⁴ mm); b.p. 141-142° (2 mm); 2.8 g (56%); n²⁰_D 1.5243; d²⁰₄ 1.1319; found MR 65.00; calculated MR 64.81. Found: C 39.9; 39.7; H 7.1; 7.0; P 13.0; S 26.2; 26.1%. C₈H₁₇PS₂O₂. Calculated: C 40.0; H 7.1; P 12.9; S 26.7%.

The O-ethyl-S-β-ethylmercaptoethyl ester of β-ethoxyethylthiophosphinic acid (XIV).

A mixture of 4 g of the O-ethyl-S-β-ethylmercaptoethyl ester of vinylthiophosphinic acid (XII), 40 ml of absolute ethyl alcohol and several drops of a solution of sodium alcoholate were heated in sealed glass tubes for 1 hour at 100°. After removal of the alcohol, the residue was dissolved in benzene; the solution was washed with cold water and dried over sodium sulfate. After distillation, a substance was obtained with b.p. 110-112° (1 · 10⁻⁴ mm); 2.2 g (46%); n²⁰_D 1.5000; d²⁰₄ 1.1125; found MR 75.65; calculated MR 76.12. Found: C 41.8; 42.1; H 8.1; 8.2; + 10.8; 10.6; S 21.9; 21.9%. C₁₀H₂₃PO₃S₂. Calculated: C 41.9; H 8.1; P 10.8; S 22.4%.

The O-ethyl-O-β-ethylmercaptoethyl ester of β-ethoxyethylthiophosphinic acid (XIII).

This was obtained from 5 g of the O-ethyl-O-β-ethylmercaptoethyl ester of vinylthiophosphinic acid (IX), 45 ml of ethyl alcohol and sodium alcoholate in the same way as was the product of the preceding experiment; b.p. 85-86.5° (1 · 10⁻⁴ mm); 3.1 g (52.5%); n²⁰_D 1.4980; d²⁰₄ 1.1172; found MR 75.13; calculated MR 76.44. Found: C 41.7; 41.7; H 8.1; 8.0; P 10.5; 10.6; S 22.7; 22.6%. C₁₀H₂₃PO₃S₂. Calculated: C 41.9; H 8.1; P 10.8; S 22.4%.

SUMMARY

Vinylthiophosphinic acid and some of its derivatives were synthesized.

LITERATURE CITED

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3. M. I. Kabachnik and N. N. Godovikov, *Dokl. AN SSSR* 110, 217 (1956).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

A NEW METHOD OF OBTAINING TETRAACYLOXY DERIVATIVES OF ZIRCONIUM

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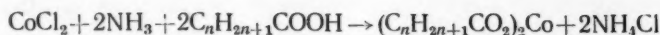
Original article submitted February 6, 1960

Interest in the metallic salts of fatty carboxylic acids is connected with the broad practical possibilities of their use [1, 2]. Metallic salts of organic acids play a special role as catalysts in the process of oxidation of organic compounds [3, 4]. Salts of metals with variable valence are effective catalysts for processes of polymerization [5]. It is also known that the stability of polymers to light is increased by the addition of some salts of organic acids [6]. Some metallic salts of fatty acids are used as antiseptic and bactericidal media and have found wide use in the pharmacological field [1].

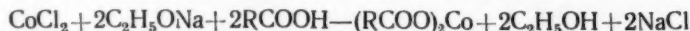
On the basis of patent data [7], one may conclude that salts of zirconium with organic acids can be used as lubricants, fuel additives, and for conferring hydrophobic properties on materials.

Metallic salts of the higher acids are soluble in the majority of organic solvents, and when the solutions are cooled they form gels or pastes; this increases the difficulty of their purification and identification. One cannot successfully obtain chemically pure neutral salts of the transition metals with organic acids by the methods available in the literature; usually mixtures of basic salts of the metals are obtained, sometimes of inconstant composition. Notwithstanding the great interest in these compounds, as far as is known to us, only for cobalt, manganese, titanium, and zirconium has anyone studied the possibility of obtaining chemically pure, neutral salts.

Two methods have been recommended for the preparation of the acyloxy derivatives of cobalt: the first method [8] consists in the interaction of dry CoCl_2 , fatty acids and ammonia in an absolute alcohol medium according to the scheme



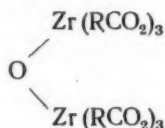
The authors proposed the use of this reaction for the preparation of the salts of cobalt with n greater than 11. The authors suggested another method for obtaining the diacyloxy derivatives of cobalt with the lower acids [9]; this consisted in the action of sodium alcoholate and fatty acids on the dry cobalt salt



As for the tetraacylates of titanium $\text{Ti}(\text{OCOR})_4$, it was not possible to obtain them by the interaction of titanium tetrachloride or orthoalkyl titanium compounds with organic acids or with acetic anhydride [10-13]. The communication of Ryan and Pletcher on the preparation of titanium tetraacylates by the action of organic acids (stearic, linoleic) on titanium tetrachloride in the presence of calcium carbonate has also been refuted [11].

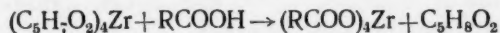
The attempts of several authors to obtain tetraacyloxy derivatives of zirconium, both by exchange reactions of zirconium salts with sodium soaps [14] (for example, sodium oleate or sodium stearate) and by the interaction of zirconium salts with acids in the presence of a coupling agent [15] led to the basic salts.

The interaction of tetraisopropoxy zirconium with an excess of the fatty acids - capronic, lauric, palmitic, and stearic - led to hexaacyloxy dizirconium oxides [15]



The authors of [16] said that by heating zirconium tetrachloride with myristic, palmitic and stearic acids for many hours in a benzene medium there occurred a slow evolution of HCl, and products were obtained which upon analysis for zirconium content corresponded to the tetraacyloxy derivatives of zirconium. An analogous method was recommended for obtaining the neutral salts of manganese [17].

The possibility of obtaining the tetraacyloxy derivatives of zirconium by means of the interaction of zirconium tetraacetylacetonate with fatty carboxylic acids was studied by the authors of this article. When organic acids are heated with the tetraacetylacetonate of zirconium they react with the evolution of acetylacetonate to form neutral salts according to the scheme



The reaction proceeds with quantitative yield in 3-8 hours. Reactions between zirconium tetraacetylacetonate and valeric, capronic and oenanthic acids were carried out in a stream of dry nitrogen with an excess of the acid. The liquid substances obtained crystallized on standing; they are subject to partial decomposition when an attempt is made to distill them in a high vacuum. The interaction of zirconium tetraacetylacetonate with ω -chloroundecanoic, lauric, palmitic, and stearic acids was realized with molar ratios of the components (1: 4) in benzene medium or in octane. Zirconium tetrapalmitate and tetrastearate are obtained in the form of light powders. These compounds partially decompose when an attempt is made to recrystallize them. However, on the positive side of this synthesis is the fact that the products separated from the reaction mixture are analytically pure without additional purification as is shown by analyses for C, H, Zr, and Cl.

The exchange of the acetylacetonate group for the acyloxy group takes place also with the corresponding compounds of manganese and cobalt; in the case of the interaction of manganese triacetylacetonate and of cobalt triacetylacetonate with palmitic and stearic acids, this exchange leads to the formation of manganese dipalmitate, manganese distearate, and cobalt distearate. The latter compound was obtained also by the interaction of the diacetylacetonate of cobalt with stearic acid in a stream of dry nitrogen.

EXPERIMENTAL PART

Zirconium Tetrastearate. A benzene solution of 1 g (0.002 M) of zirconium tetraacetylacetonate was added to 2.33 g (0.009 M) of stearic acid. A mixture of acetylacetone and the solvent was distilled from the reaction milieu by heating from 90-130° while dry air was passed through and the pressure was gradually lowered to 20 mm. The reaction was finished in 3 hrs. (A sample of the reaction mixture did not become colored when treated with FeCl_3). The reaction mixture was heated for an additional hour at 130°/13 mm. A light powder was obtained, 2.5 g, (100% of the theoretical yield), which gave an analysis corresponding to zirconium tetrastearate. Found: C 70.32; 70.92; H 11.43; 11.61; Zr 7.26; 7.33%. $(\text{C}_{18}\text{H}_{35}\text{O}_2)_4\text{Zr}$. Calculated: C 70.59; H 11.52; Zr 7.45%. After recrystallization from hexane the product had a lowered carbon content in comparison with that calculated for zirconium tetrastearate. Found: C 69.39; 69.35; H 11.37; 11.27; Zr 7.32; 7.52%.

Zirconium tetrapalmitate. A mixture of zirconium tetraacetylacetonate, 1.0 g (0.002 M) of palmitic acid, 2.10 g (0.008 M) was wet with 5 ml of benzene. The experiment was carried out in a fashion analogous to that preceding. There was obtained 2.25 g (100% of the theoretical) of a light powder. Found: C 69.39; 69.25; H 11.30; 11.39; Zr 8.02; 8.18%. $(\text{C}_{16}\text{H}_{31}\text{O}_2)_4\text{Zr}$. Calculated: C 69.06; H 11.23; Zr 8.18%. On recrystallization from hexane the zirconium tetrapalmitate partially decomposed.

Zirconium tetralaurate. The experiment was carried out in a fashion analogous to that preceding. The reaction was finished after 11 hours. From 1.64 g was obtained 1.8 g (100% of the theoretical) of a waxy substance which on analysis corresponded to zirconium tetralaurate. Found: C 64.32; 64.20; H 10.41; 10.60; Zr 10.12; 10.30%. $(\text{C}_{12}\text{H}_{23}\text{O}_2)_4\text{Zr}$. Calculated: C 64.87; H 10.44; Zr 10.28%. After recrystallization from hexane at -30°: Found: C 64.75; 64.60; H 10.86; 10.54; Zr 9.42; 9.27%.

Zirconium tetra- ω -chloroundecanoate. A benzene solution of 1 g (0.002 M) of zirconium tetraacetylacetonate and 1.81 g (0.008 M) of ω -chloroundecanoic acid was heated to 120°; the distillation of the mixture of benzene and acetylacetonate was carried out during 4.5 hours, at normal pressure; the reaction was continued at 120°-140° with the passage of a stream of dry air. After the reaction was finished, which required 12.5 hrs, traces of the solvent were removed at 1 mm and 130° during 20 min. A viscous liquid was obtained weighing 1.95 g (a quantitative yield). Found: C 54.48; 54.58; H 8.52; 8.45; Zr 9.68; 9.55; Cl 14.45; 14.32%. $(\text{C}_{11}\text{H}_{20}\text{O}_2\text{Cl})_4\text{Zr}$. Calculated: C 54.49; H 8.32; Zr 9.40; Cl 14.63%.

An analogous experiment was carried out in octane as a medium; the reaction was finished after 6 hrs. Found: C 55.05; H 8.88; Zr 9.33%.

Zirconium tetraoentanate. Zirconium tetraacetylacetonate, 2 g (0.004 M) was wet with 15 ml of oenanthalic acid. The distillation of the mixture was acetylacetone and unreacted oenanthalic acid was carried in a stream of dry nitrogen at 140°-150° and 130 mm, with gradual lowering of the pressure to 30 mm. After 8.5 hrs the reaction was finished. The traces of oenanthalic acid which had not entered into the reaction was removed at 1 mm and 120-130°. There was obtained a rather mobile liquid which was shown by analysis to correspond to zirconium tetraoentanate. Found: C 55.52; 55.63; H 8.75; 8.67; Zr 14.54; 14.56%. $(C_7H_{13}O_2)_4Zr$. Calculated: C 55.30; H 8.61; Zr 15.02%. By distillation in vacuo at approximately 10^{-4} mm, the substance decomposed with the formation of oenanthalic acid.

Zirconium tetravalerate. The interaction between zirconium tetraacetylacetonate (4 g) and an excess of valeric acid (20 ml) was realized in a fashion analogous to that of the preceding experiment. The reaction was carried out in 3.5 hrs. There was obtained 4.06 g (100%) of the theoretical of a rather viscous liquid which gradually solidified. Found: C 48.28; 48.40; H 7.22; 7.16; Zr 19.00; 18.65%. $(C_5H_9O_2)_4Zr$. Calculated: C 48.44; H 7.32; Zr 18.41%. The product recrystallized from hexane with partial decomposition. Found: C 47.51; H 7.19; Zr 18.10%.

Zirconium tetracapronate. The reaction between zirconium tetraacetylacetonate (4 g) and an excess of capronic acid was carried out in a fashion analogous to that of the preceding experiment. After 3 hrs a sample from the reaction flask did not give a color with ferric chloride. Zirconium tetracapronate was obtained in quantitative yield (4.38 g) in the form of a viscous liquid. Found: C 51.66; H 7.98; Zr 16.86%. $(C_6H_{11}O_2)_4Zr$. Calculated: C 52.22; H 8.03; Zr 16.54%.

The interaction of cobalt triacetylacetonate with stearic acid. A solution of 1 g (0.0028 M) of cobalt triacetylacetonate in xylene was added to a solution of 2.4 g (0.0084 M) of stearic acid in xylene. This was heated at 165° for 15 min, and afterward the distillation of the mixture of the solvent and acetylacetone was carried out at 116° while dry air was passed through. The reaction was continued in all for 18 hrs. There was obtained 2.8 g of a powder quite soluble in hot benzene, hexane, and chloroform. The product which was apparently cobalt distearate was recrystallized from hexane. A rose powder was obtained. Found: C 69.06; 68.92; H 11.20; 11.25%. $(C_{18}H_{35}O_2)_2Co$. Calculated: C 69.07; H 11.28%.

The interaction of cobalt diacetylacetonate and stearic acid. A xylene solution of stearic acid, 2.81 g (0.01 M), and 1.28 g (0.005 M) of cobalt diacetylacetonate was heated to 158-160°; the distillation of the acetylacetone and the solvent was carried in a stream of nitrogen. After 5 hrs the reaction was finished. The product was obtained in the form of a paste. After recrystallization from hexane there was obtained 1.62 g (51.6% of the theoretical) or rose colored crystals. Found: C 69.42; H 11.39%. $(C_{18}H_{35}O_2)_2Co$. Calculated: C 69.07; H 11.28%.

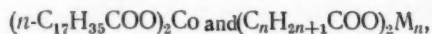
The interaction of manganese triacetylacetonate and stearic acid. A xylene solution of manganese triacetylacetonate, 1.17 g (0.0033 M) and 2.84 g (0.01 M) of stearic acid was heated to 160° for the distillation of a mixture of acetylacetone and solvent. The reaction was finished after 10 hours. The black solid product was recrystallized from chloroform; it was washed with hexane and dry ether, and was dried at 1 mm and 45° for 2 hrs.; the product weighed 1.86 g. Found: C 69.86; H 11.22%. $(C_{18}H_{35}O_2)_2Mn$. Calculated: C 69.50; H 11.37%.

The interaction of manganese triacetylacetonate with palmitic acid. The experiment was carried out analogously to the preceding. From 1.17 g (0.0033 M) of manganese triacetylacetonate and 2.56 g (0.01 M) of palmitic acid there was obtained 4.39 g of a black solid mass, not soluble in hexane and alcohol, soluble in chloroform. The reaction was continued for 11 hours. The product was recrystallized from chloroform, washed with hexane, and dried for several hours with dry air. There was obtained 1.27 g of a gray powder, by analysis corresponding to manganese dipalmitate. Found: C 67.66; 67.72; H 10.80; 10.63%. $(C_{16}H_{31}O_2)_2Mn$. Calculated: C 67.91; H 11.05%.

SUMMARY

1. By the exchange reactions of zirconium tetraacetylacetonate with carboxylic acids there were obtained the tetraacyloxy derivatives of composition $[X(CH_2)_nCOO]_4Zr$, where $n = 4, 5, 6, 10, 11, 15, 17$; $X = H, Cl$.

2. By the interaction of cobalt triacetylacetonate and manganese triacetylacetonate with stearic and palmitic acids there were obtained the diacyloxy derivatives of composition



where $n = 15, \text{ or } 17$.

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PROPENYL STEREOISOMERS OF TRI- AND PENTAVALENT ANTIMONY

A. N. Nesmeyanov, A. E. Borisov and N. V. Novikova

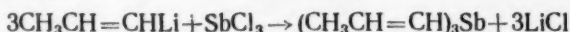
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

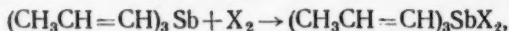
No. 4, pp. 612-617, April, 1961

Original article submitted February 29, 1960

Continuing our work on the investigation of organometallic compounds of the ethylene series [1-3] we can report in greater detail [4] on the synthesis of a series of stereoisomeric propenyl compounds of antimony, of the type R_3Sb , R_5Sb , R_4SbX and R_3SbX_2 . Cis and trans-propenyllithium, prepared from cis and trans-propenyl bromide respectively with lithium metal [3], react smoothly with antimony trichloride, forming tri-(cis-) and tri-(trans-propenyl) antimony respectively



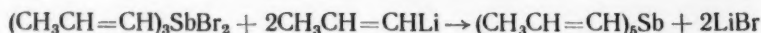
The reaction of these two substances with halides led to a series of stereoisomeric compounds of pentavalent antimony



where $X = Cl, Br$ or I .

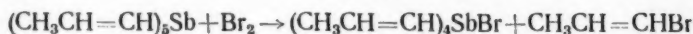
During this process, liquid tri-(trans-propenyl) antimony dichloride and dibromide were obtained from the reaction products of tri-(trans-propenyl) antimony with chlorine and bromine respectively. With the same halides the corresponding cis-isomer gave crystalline tri-(cis-propenyl) antimony dichloride and dibromide. In contrast to the case of stereoisomers of β -chlorovinyl compounds of antimony (and also of mercury and tin), here the trans-compounds are liquid at room temperature, while the cis-compounds are crystalline.

The same dihalide derivatives of the cis- and trans-tri-(propenyl) antimony dichloride were obtained from the reaction products of cis- and trans-tripropenylantimony with thallium trichloride. Both stereoisomers of pentapropenylantimony



were synthesized by the action of the corresponding stereoisomers of propenyllithium on the cis- and trans-stereoisomers of tri-(propenyl) antimony dibromide. Initial attempts to isolate these compounds by vacuum distillation were unsuccessful, as was the case with attempts to obtain pentamethyl compounds of antimony [5]. Trivalent antimony compounds: tri-(trans-) and tri-(cis-propenyl)antimony were the main distillation product. We succeeded in separating pentapropenyl compounds of antimony by extracting the reaction mass with petroleum ether, followed by its distillation. As was shown by the analysis, we obtained fairly pure substances. The isomers have different refractive indices - the cis-isomer n_D^{20} 1.5610, and the trans-isomer n_D^{20} 1.5490 - and different infrared absorption spectra.

When pentapropenyl compounds of antimony were treated with an equimolecular amount of bromine, two stereoisomeric tetrapropenylstibonium bromides were obtained, as follows



These substances have different melting points: the compound obtained from cis-pentapropenylantimony had a m.p. of 140-143°, while that obtained from trans-pentapropenylantimony melted at 45-48°; they also have different infrared absorption spectra.

The configurations of these compounds were determined on the basis of the infrared absorption spectra. A trans-configuration was assigned to compounds with a higher vibrational frequency in the region of the $C=C$ double bond and a vibrational frequency in the 950-980 cm^{-1} region, while compounds with a lesser vibrational frequency in the

Formula of the substance	Characteristic vibrational frequencies of the infrared spectrum, cm ⁻¹	
	cis	trans
(CH ₃ CH=CH) ₃ Sb	920 W, 970 W, 1182 M, 1615 M	935 M, 970 S, 1068 M 1200 S, 1620 S
(CH ₃ CH=CH) ₃ SbCl ₂	923 W, 1200 W, 1600 W	955 S, 1070 M, 1188 S, 1615 S
(CH ₃ CH=CH) ₃ SbBr ₂	925 W, 1600 W	953 S, 1068 M, 1188 S, 1620 S
(CH ₃ CH=CH) ₄ SbBr	925 W, 1600—1610 M	965 S, 1068 S, 1190 S, 1620 S
(CH ₃ CH=CH) ₃ SbJ ₂	928 W, 1470 S, 1610 M	948 S, 1065 M, 1625 S
(CH ₃ CH=CH) ₅ Sb	920 W, 974 W, 1200 W, 1595 S	972 S, 1068 M, 1185 M, 1600 S

* W = weak; M = medium; S = strong.

region of the C=C double bond and without vibrational frequencies in the 950-980 cm⁻¹ region were included in the cis-series. The infrared absorption spectrum (see table) of cis-tripropenylantimony and cis-pentapropenylantimony indicates the presence of a very small admixture of the trans isomer. This assumption is based on the presence of very weak lines of the vibrational frequencies of the infrared spectrum: 970 cm⁻¹ for the first compound, and 974 cm⁻¹ for the second.

To obtain a more accurate representation of the configurations of these compounds, we investigated the infrared absorption spectrum of the initial cis-propenyl bromide; it contains a frequency of 985 cm⁻¹ of approximately the same intensity. In the case of trans-propenyl bromide a wide and intense frequency of 920-950 cm⁻¹ was found in this region. This confirms our representations of the configurations, which also agree with the law we previously established [1-3].

EXPERIMENTAL

Tri-(trans-propenyl)antimony. Trans-propenyllithium was obtained from 20 g (0.1653 M) of trans-propenyl bromide and 2.2 g (0.3100 M) of lithium metal in 150 ml of absolute ether at 5-7°. A solution of 10 g (0.0438 M) of antimony trichloride in 50 ml of absolute ethyl ether was added at 10-20° to the reagent obtained (period of addition, 40 minutes). After the reaction mass had been stirred for 4 hours at 15-20°, it was decomposed with 150 ml of a saturated ammonium chloride solution at 4-6°. The ethereal solution was separated, dried with anhydrous CaCl₂ and distilled under the vacuum (in the usual way). The following fractions were collected: fraction I with a b.p. of up to 82° (5 mm); 0.51 g; n_D²⁰ 1.5510; fraction II with a b.p. of up to 82° (5 mm); 9.0 g (83% of theoretical); n_D²⁰ 1.5511; d₄²⁰ 1.2870; residue 1.0 g. Found: C 43.92; 43.99; H 6.03; 6.05%. C₉H₁₅Sb. Calculated: C 44.12; H 6.17%.

Tri-(cis-propenyl)antimony. Cis-propenyllithium was reacted with antimony trichloride under the conditions described above. From 20.0 g (0.1653 M) of propenyl bromide, 2.2 g (0.3100 M) of lithium metal and 10 g (0.0438 M) of SbCl₃ we obtained after corresponding treatment and vacuum distillation the following fractions: fraction I with a b.p. of up to 70° (4-5 mm); 0.7 g; n_D²⁰ 1.5580; fraction II with a b.p. of up to 70° (4-5 mm); 7.7 g (71% of the theoretical); n_D²⁰ 1.5590; d₄²⁰ 1.3092; residue 0.9 g. Found: C 44.08; 44.21; H 6.16; 6.23%. C₉H₁₅Sb. Calculated: C 44.12; H 6.17%.

Trans- and cis-tripropenylantimony are liquid substances which become turbid in air; they can be kept for a considerable period in sealed ampoules in the cold.

Tri-(trans-propenyl)antimony dibromide. A cooled (to 0°) solution of 1.3 g (0.0081 M) of bromine in 10 ml of chloroform was added dropwise with stirring to a solution of 2.0 g (0.0081 M) of tri-(trans-propenyl)antimony in 10 ml of dry chloroform, cooled to 0°. When the chloroform had been evaporated, the residue was distilled under

vacuum. The following fractions were obtained: fraction I with a b.p. of up to 166° (4 mm); 0.3 g; n_D^{20} 1.6290; fraction II with a b.p. of up to 166-167° (4 mm); 2.5 g (75% of the theoretical); n_D^{20} 1.6270; d_4^{20} 1.8596; fraction III with a b. p. of up to 167-168.5° (4 mm); 0.15 g; n_D^{20} 1.6275. Found: C 26.76; 26.70; H 3.80; 3.81; Br 39.05; 38.81%. $C_9H_{15}SbBr_2$. Calculated: C 26.70; H 3.73; Br 39.48%.

Tri-(trans-propenyl)antimony dibromide becomes turbid in air; it is readily soluble in methanol, ethanol, acetone, chloroform, and ether, and insoluble in petroleum ether.

Tri-(cis-propenyl)antimony dibromide. The reaction of tri-(cis-propenyl)antimony with bromine was carried out under the same conditions and with the same amounts as for the trans-isomer. After the chloroform had been evaporated, the solid residue was recrystallized from 10 ml of ether. We obtained 2.31 g (70% of the theoretical yield) of the substance (transparent rhombic prisms with an m.p. of 85-86°). Found: C 26.65; 26.56; H 3.68; 3.67; Br 40.74; 40.85%. $C_9H_{15}SbBr_2$. Calculated: C 26.70; H 3.73; Br 39.48%.

Tri-(cis-propenyl)antimony dibromide is readily soluble in methanol, ethanol, acetone, chloroform, and benzene; it is moderately soluble in ether and insoluble in petroleum ether.

Reaction of tri-(cis-propenyl)antimony with thallium trichloride. A solution of 1.268 g (0.0040 M) of thallium trichloride in 5 ml of ether was added to 1.0 g (0.0040 M) of tri-(trans-propenyl)antimony in 5 ml of ether. A white precipitate of thallium monochloride was immediately formed; after it had been washed with ether and dried, it weighed 0.96 g (98% of the theoretical). After the solvent had been distilled, the sirupy liquid was distilled under vacuum. We obtained 0.84 g (65% of the theoretical yield) of a liquid substance (n_D^{20} 1.5820, d_4^{20} 1.5056) at 160-162° (4 mm).

Tri-(trans-propenyl)antimony dichloride is readily soluble in methanol, ethanol, acetone, and chloroform; it is soluble in ether but insoluble in petroleum ether. Found: C 33.98; 33.98; H 4.62; 4.71; Cl 22.52; 22.74%. $C_9H_{15}SbCl_2$. Calculated: C 34.22; H 4.79; Cl 22.45%.

Reaction of tri-(cis-propenyl)antimony with thallium trichloride. Under similar conditions to those for the trans-isomer, from 1.0 g (0.0040 M) of tri-(cis-propenyl)antimony and 1.268 g (0.0040 M) of thallium trichloride we obtained 0.94 g (96% of the theoretical yield) of thallium monochloride and 1.1 g of a solid substance, which after recrystallization from 5.0 ml of ether had an m.p. of 74-75°; the weight was 0.92 g (71% of the theoretical yield). The substance was very readily soluble in methanol, ethanol, acetone, and chloroform, moderately soluble in ether and insoluble in petroleum ether. Found: C 34.02; 34.00; H 4.63; 4.76; Cl 22.58; 22.47%. $C_9H_{15}SbCl_2$. Calculated: C 34.22; H 4.79; Cl 22.45%.

Tri-(trans-propenyl)antimony dichloride. Chlorine was passed at a rate of 90 bubbles per minute into a solution of 2.0 g (0.0081 M) of tri-(trans-propenyl)antimony in 15 ml of chloroform at 0° with stirring, until a faint greenish color was formed and the odor of the initial compound had disappeared. When the chloroform had been evaporated, the liquid sirupy residue was distilled under vacuum. The following fractions were collected: Fraction I with a b.p. of up to 155° (2 mm); 0.18 g; n_D^{20} 1.5837; fraction II with a b.p. of up to 155-156° (2 mm); 1.85 g (71% of the theoretical); n_D^{20} 1.5822. The n_D^{20} for the above-described tri-(trans-propenyl)antimony is 1.5820.

Tri-(cis-propenyl)antimony dichloride. The experiment was carried out under the conditions described for tri-(trans-propenyl)antimony. After chlorination, a solid substance was obtained from 2.0 g (0.0081 M) of tri-(cis-propenyl)antimony. After recrystallization from 10 ml of ether, 1.84 g (71% of the theoretical yield) of a substance (transparent prisms, m.p. 73.5-75°) was obtained. The above-described tri-(cis-propenyl)antimony dichloride melts at 74-75°.

Reaction of tri-(trans-propenyl)antimony with iodine. A solution of 1.04 g (0.0040 M) of iodine in 15 ml of ether was added to 1.0 g (0.0040 M) of tri-(trans-propenyl)antimony in 5 ml of ether at 0°. A yellow color, which did not fade immediately, appeared when ~85-90% of the theoretical amount of iodine had been consumed. After evaporation of the ether (under nitrogen), 1.90 g of a cherry-colored liquid was obtained. The substance was washed with an aqueous solution in hyposulfite, and water, and was dried with calcined calcium chloride; the weight was 1.63 g (84% of the theoretical).

Reaction of tri-(cis-propenyl)antimony with iodine. The reaction of tri-(cis-propenyl)antimony with iodine was carried out under similar conditions and with the same amounts. Complete addition of iodine was indicated by a yellow color which appeared when the theoretical amount of iodine had been consumed.

After part of the ether had been evaporated, we obtained 1.64 g (80.5% of the theoretical) of a substance with an m.p. of 122-123°. Found: C 22.07; 22.03; H 3.19; H 3.13%. $C_9H_{15}SbI_2$. Calculated: C 21.67; H 3.03%. After all the ether had been evaporated we obtained a further 0.37 g of a crystalline cherry-colored substance with an m.p. of 110-117°.

Synthesis of penta-(trans-propenyl)antimony. Trans-propenyllithium, obtained, from 0.7 g (0.1009 M) of lithium metal in 50 ml of ether and 6.0 g (0.05 M) of trans-propenyl bromide in 6.0 ml of dry ether at 5-7°, was added dropwise to a solution of 8.0 g (0.0197 M) of tri-(trans-propenyl)antimony dibromide in 25.0 ml of ether at -10-5° for 45 minutes. After the reaction mass had been stirred for 3 hours at this temperature, the ester was evaporated at the pump, without heating. The residue in the flask was extracted repeatedly (4-6 times) with petroleum ether (b.p. 35-40°). The precipitate was filtered on a Schott funnel; it was soluble and non-combustible. Petroleum ether was evaporated from the filtrate at the pump, without heating. The liquid residue was filtered through a multi-layer filter. We obtained 5.00 g (77% of the theoretical yield) of a liquid transparent colorless substance with n_D^{20} 1.5490, d_4^{20} 1.17025. Its aqueous solution was alkaline to litmus. Found: C 55.68; 55.69; H 7.82; 8.01%. $C_{15}H_{25}Sb$. Calculated: C 55.07; H 7.7%.

Penta (trans-propenyl)antimony is readily soluble in petroleum ether, benzene, chloroform, ether, acetone, and alcohol.

Penta-(cis-propenyl)antimony. Under the same conditions and with the same amounts of reagents described for penta-(trans-propenyl)antimony we obtained 5.17 g (80% of the theoretical yield) of a colorless liquid substance; n_D^{20} 1.5610; d_4^{20} 1.19723. An aqueous solution of the substance was alkaline to litmus. Found: C 55.56; 55.79; H 7.97; 7.88%. $C_{15}H_{25}Sb$. Calculated: C 55.07; H 7.7%. Penta-(cis-propenyl)antimony is readily soluble in petroleum ether, ether, benzene, chloroform, and alcohol.

All operations for the preparation of penta-(trans-propenyl)antimony and penta-(cis-propenyl)antimony (synthesis evaporation of solvents, filtration) were carried out in a current of pure dry nitrogen.

Trans-tetrapropenylstibonium bromide. A solution of 0.48 g (0.003 M) of bromine in 5.0 ml of chloroform was added dropwise to 1.0 g (0.003 M) of penta-(trans-propenyl)antimony in 5.0 ml of chloroform. When the chloroform had been evaporated (in a current of nitrogen at the pump), the slightly turbid liquid residue was passed through a multilayer filter. A transparent liquid (1.05 g), which crystallized out in a day, was collected. The crystals were filtered (with cooling), washed with the minimum quantity of cold ether, and dried in a desiccator over $CaCl_2$. We obtained 0.88 g (78% of the theoretical yield) of a white crystalline substance with an m.p. of 45-48°. Found: C 39.18; 39.03; H 5.72; 5.56%. $C_{12}H_{20}SbBr$. Calculated: C 39.38; H 5.51%. The substance was very readily soluble in water, alcohol, acetone, and chloroform, and less soluble in ether.

Cis-tetrapropenylstibonium bromide. The experiment was carried out under conditions similar to those described for the trans-isomer. After the chloroform had been evaporated, the solid residue was dissolved in 2 ml of chloroform and precipitated with 5.0 ml of dry ether. From 1.0 g (0.003 M) of penta-(cis-propenyl)antimony and 0.48 g (0.003 M) of bromine we obtained 0.8 g (71% of the theoretical yield) of fine lustrous plates with an m.p. of 140-143°. Found: C 39.25; 39.19; H 5.53; 5.37%. $C_{12}H_{20}SbBr$. Calculated: C 39.38; H 5.51%. The substance was very readily soluble in water, alcohol, acetone, and chloroform, and difficultly soluble in ether.

We wish to express our thanks to I. V. Obreimov and N. A. Chumaevskii for determining the infrared spectra.

SUMMARY

1. The geometrical isomers of propenylantimony were synthesized for the first time, by reacting cis- and trans-propenyllithium with antimony trichloride; their reaction with the halogens Cl, Br, and I and thallium trichloride led to a series of isomeric compounds of pentavalent antimony.
2. Liquid stereoisomers of pentapropenylantimony were synthesized from the cis- and trans-isomers of tripropenylantimony dibromide and the corresponding isomers of propenyllithium.
3. When these isomers were treated with a specific amount of bromine, isomeric compounds of tetrapropenylstibonium bromide are formed.
4. The configurations of the propenyl compounds of tri and pentavalent antimony obtained by the authors were determined on the basis of the infrared absorption spectra.

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FLUORINE-CONTAINING β -SULTONESCOMMUNICATION 5. REACTION OF TETRAFLUOROETHANE- β -PYROSULTONE WITH ALCOHOLS

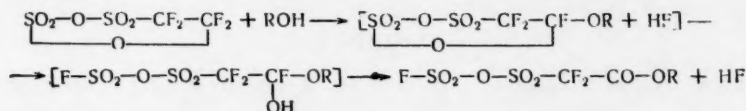
G. A. Sokol'skii, M. A. Dmitriev and I. L. Knunyants

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 4, pp. 617-620, April, 1960

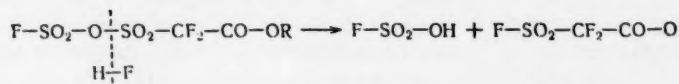
Original article submitted February 29, 1960

It was previously shown that during alcoholysis of fluorine-containing β -sultones, esters of the corresponding α -sulfofluoride carboxylic acids are formed [1]. Therefore it could be assumed that the reaction of tetrafluoroethane- β -pyrosultone with alcohols would give ester of pyrosulfofluoride difluoroacetic acid. In actual fact, it was found that the direction of the alcoholysis of tetrafluoroethane- β -pyrosultone depends on the order of mixing of the reagents and on the temperature conditions of the process. Thus, with careful addition of alcohol to an equimolar amount of cooled pyrosultone, two reaction products — the ester of sulfofluoride difluoroacetic acid and fluorosulfonic acid — are formed; liberation of hydrogen fluoride is not observed. On the other hand, if pyrosultone is added to excess alcohol (two or more moles) at room temperature, hydrogen fluoride is liberated and the main reaction product is the diester of sulfodifluoroacetic acid; small amounts of the ester of sulfofluoride difluoroacetic acid are also formed.

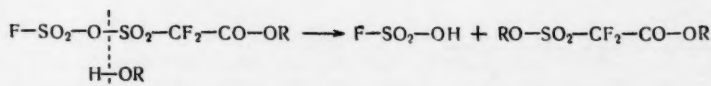
In the first stage of the alcoholysis of pyrosultone, the ester of pyrosulfofluoride difluoroacetic acid is evidently formed



This compound is unstable and tends to undergo further conversions, the direction of which depends on the composition of the reaction mixture. In the first case, i.e., in the absence of alcohol, the intermediate pyrosulfonfluoride compound reacts with hydrogen fluoride; this leads to the formation of fluorosulfonic acid and the ester of sulfonfluoride difluoroacetic acid; during this process the hydrogen fluoride is completely utilized



In the second case, i.e., in the presence of alcohol, the latter may react with the pyrosulfurfluoride compound, with the formation of the diester of sulfodifluoroacetic acid; during this process hydrogen fluoride is not involved in the reaction



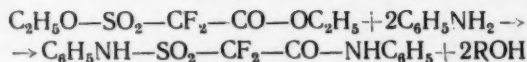
There is no doubt that both these processes of decomposition of the intermediate pyrosulfodifluoride compound are competitive. To eliminate the second process it is necessary to limit strictly the amount of alcohol involved in the reaction and cool the reaction mass to avoid the liberation of hydrogen fluoride from the latter. On the other hand, for maximum exclusion of the first process, with the object of obtaining the maximum amount of the diester of sulfodifluoroacetic acid, it is necessary to use excess alcohol. Thus, when tetrafluoroethane-8-pyrosultone reacts with two moles of methanol the yield of the diester is ~50% and ~40% of the monoester is formed as a secondary

product. When three moles of methanol are used per mole of pyrosultone the diester yield reaches 74%, and the amount of monoester falls to 22%. Evidently, with a still greater excess of alcohol and with use of heating to facilitate removal of hydrogen fluoride, the first process may be practically excluded and the yield of the diester of sulfodifluoroacetic acid will be almost quantitative. In the latter case the esterification reaction of fluorosulfonic acid is also possible, whereas with a limited amount of alcohol there probably occurs practically complete deesterification by hydrogen fluoride, which can form methyl fluorosulfate.

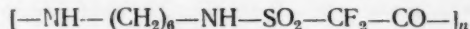
Thus, when tetrafluoroethane- β -pyrosultone reacted with methanol, ethanol and *n*-butanol we obtained the dimethyl-, diethyl and di-*n*-butyl esters of sulfodifluoroacetic acid were obtained. The structure of these esters was proven by various methods. Thus, when they are dissolved in aqueous alkalis two equivalents of alkali are consumed and neither fluorine nor sulfate ions are detected in the solution



The diesters of sulfodifluoroacetic acids react with primary and secondary amines, the corresponding diamides being formed; for example,



When dibasic amines are used, the corresponding polyamides are formed, for example



It is of interest to note that the polyamide obtained from the dimethyl or diethyl ester of sulfodifluoroacetic acid and hexamethylenediamine is a colorless vitreous mass, resistant to hydrolysis and heat — it only softens at a temperature above 200° — and is not ignited in the flame of a gas burner. For this reason, polyamides of this type may be used for obtaining various plastics.

EXPERIMENTAL

Action of methanol on tetrafluoroethane- β -pyrosultone. A quantity of 3.2 g of dry methanol was added dropwise with shaking to 26.0 g of tetrafluoroethane- β -pyrosultone with cooling to -20°. The mixture was kept in the cold for an hour and was then gradually heated to room temperature. Double fractionation gave 17.7 g of the methyl ester of sulfofluoride difluoroacetic acid (92%) with a b.p. of 113-115°; d_{20}^{20} 1.5150; n_D^{20} 1.3502 (literature data give b.p. 115°; d_{20}^{20} 1.5159; n_D^{20} 1.3510) and 7.6 g of fluorosulfonic acid (76%) with a b.p. of 163-165°; d_{20}^{20} 1.7392 (literature data give a b.p. of 165.5°; d_{15}^{15} 1.743).

Dimethyl ester of sulfodifluoroacetic acid. A quantity of 26.0 g of tetrafluoroethane- β -pyrosultone was added dropwise with shaking to 12 ml of dry methanol at 0°. The reaction mixture was heated gradually for an hour to room temperature (18-20°) and was carefully poured onto 30 g of ice. The lower layer was separated, washed with ice water and dried over magnesium sulfate. Double fractionation gave 4.3 g of the methyl ester of sulfofluoride difluoroacetic acid (22%) and 15.1 g of the dimethyl ester of sulfodifluoroacetic acid (74%) with a b.p. of 83-85° (8 mm); d_{20}^{20} 1.4895; n_D^{20} 1.3990. Found: C 23.45; H 2.74; F 18.93; S 15.43%; mol. wt. 208.0; acid equivalent 2.01. $\text{C}_6\text{H}_4\text{O}_5\text{F}_2\text{S}$. Calculated: C 23.53; H 2.94; F 18.63; S 15.69% mol. wt. 204.1; acid equivalent 2.00.

The dimethyl ester of sulfodifluoroacetic acid is a heavy oily liquid with a pleasant fruity odor; it is insoluble in water, but dissolves readily in organic solvents.

The diethyl ester of sulfodifluoroacetic acid. By a similar method, from ethanol and tetrafluoroethane- β -pyrosultone we obtained a 20% yield of the ethyl ester of sulfofluoride difluoroacetic acid with a b.p. of 128-130°, d_{20}^{20} 1.3980; n_D^{20} 1.3572 (literature data give a b.p. of 129-130°, d_{20}^{20} 1.3965, n_D^{20} 1.3565) and a 78% yield of the diethyl ester of sulfodifluoroacetic acid with a b.p. of 103-104° (8 mm); d_{20}^{20} 1.3482; n_D^{20} 1.3939. Found: C 30.82; H 4.14; F 16.85; S 13.52%; mol. wt. 228.5; acidity equivalent 1.97. $\text{C}_6\text{H}_{10}\text{O}_5\text{F}_2\text{S}$. Calculated: C 31.05; H 4.31; F 16.36; S 13.77%; mol. wt. 232.1; acidity equivalent 2.00.

Di-*n*-butyl ester of sulfodifluoroacetic acid. By a similar method, from *n*-butanol and tetrafluoroethane- β -pyrosultone we obtained a 25% yield of the *n*-butyl ester of sulfofluoride difluoroacetic acid (see below) and a 70% yield of the di-*n*-butyl ester of sulfodifluoroacetic acid with a b.p. of 122-123° (8 mm) d_{20}^{20} 1.3046; n_D^{20} 1.4615.

Found: F 12.78; S 11.32%; mol. wt. 280.5; acidity equivalent 2.03. $C_{10}H_{18}O_5F_2S$. Calculated: F 13.18; S 11.10%; mol. wt. 288.3; acidity equivalent 2.00.

N-Butyl ester of sulfofluoride difluoroacetic acid. By a method previously described [1], from n-butanol and tetrafluoroethane- β -sultone we obtained an 86% yield of the n-butyl ester of sulfofluoride difluoroacetic acid with a b.p. of 161-162°; d_4^{20} 1.2845; n_D^{20} 1.3719. Found: mol. wt. 231.0; MR 41.48; acidity equivalent 3.05; equivalent of hydrolyzable fluorine 1.02. $C_6H_9O_4F_2S$. Calculated: mol. wt. 234.6; MR 41.32; acidity equivalent 3.00; equivalent of hydrolyzable fluorine 1.00.

Dianilide of sulfodifluoroacetic acid. A solution of 2.04 g of the dimethyl ester of sulfodifluoroacetic acid and 1.86 g of freshly distilled aniline in 5 ml of methanol was heated gradually to boiling (in one hour) and was boiled for 2 hours. The solution was then diluted with 20 ml of water and the viscous oil which separated out was washed twice with hot water (10 ml at a time) and after 12 hours it had partially crystallized. The crystals were filtered at the pump and recrystallized from 8-10 ml of a mixture of water and alcohol (1: 1). We obtained 1.6 g of the crystalline dianilide of sulfodifluoroacetic acid with a b.p. of 161.5-162.5°. A mixed sample with the dianilide obtained from the ethyl ester of sulfofluoride difluoroacetic acid showed no depression of the melting point.

Polymer of hexamethylene diamide of sulfodifluoroacetic acid. A mixture of 2.04 g of the dimethyl or 2.32 g of the diethyl ester of sulfodifluoroacetic acid and 1.16 g of hexamethylenediamine was shaken vigorously for an hour at 0-5°; during this process the mixture gradually solidified. The liberated alcohol was removed by heating the mixture under vacuum. The residue (2.45 g) was the polymer of the hexamethylene diamide of sulfodifluoroacetic acid. Found: N 10.26; F 14.03; S 12.90%. $C_8H_{14}O_3N_2F_2S$. Calculated: N 10.94; F 14.85; S 12.50%.

The polymer was a colorless transparent vitreous mass; it was insoluble in water, alcohol, acetone, benzene, chloroform and carbon tetrachloride; it softened at 200° and was not ignited in the flame of a gas burner.

SUMMARY

1. The reaction between tetrafluoroethane- β -pyrosultone and alcohols was investigated and the dimethyl, diethyl and di-n-butyl esters of sulfodifluoroacetic acid were obtained.
2. A new type of polyamide was obtained by reacting the diesters of sulfodifluoroacetic acid with hexamethylenediamine.

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1. M. A. Dmitriev, G. A. Sokol'skii and I. L. Knunyants, *Izvestiya Akad. Nauk SSSR. Otd. Khim. Nauk* 1227 (1960).

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FLUORINE-CONTAINING β -SULTONES

COMMUNICATION 6. SULFOFLUORIDE MONOFLUOROACETIC ACID

G. A. Sokol'skii, M. A. Dmitriev and I. L. Knunyants

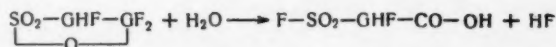
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 4, pp. 621-622, April, 1961

Original article submitted March 5, 1960

It was previously reported [1] that sulfofluoride difluoroacetic acid was obtained by controlled hydrolysis of tetrathioethane- β -sulfone acid. It may be assumed that various substituted α -sulfofluoride carboxylic acids may be obtained by the same method from other fluoride-containing β -sultones. The present communication gives the results of a similar investigation of sulfofluoride monofluoroacetic acid and some of its derivatives.

When α -hydrotrifluoroethane- β -sultone was treated with an equimolar amount of water, a vigorous reaction was observed, accompanied by an increase in the temperature of the mixture, liberation of hydrogen fluoride and partial crystallization. After the hydrogen fluoride had been driven off and the residue had been recrystallized, crystalline sulfofluoride monofluoroacetic acid was precipitated, formed by the reaction



Sulfofluoride monofluoroacetic acid is an extremely hygroscopic compound and forms a stable dihydrate with water. Like its difluoro-substituted analog, the acid forms a series of derivatives. Thus, when sulfofluoride monofluoroacetic acid was treated with phosphorus pentoxide a quantitative yield of the acid anhydride was obtained, while treatment with phosphorus pentachloride gave the acyl chloride; reaction with alcohols converted the latter to acid esters identical to the esters obtained by alcoholysis of α -hydrotrifluoroethane- β -sultone [2]. The physical properties of sulfofluoride monofluoroacetic acid and some of its derivatives are given in the table.

Formula	B.p., °C (p, mm Hg)	d_4^{20}	n_D^{20}
F---SO ₂ ---CHF---CO---OH	88-90° (14); M.p. 48-49	—	—
F---SO ₂ ---CHF---CO---OH·2H ₂ O	112-113 (14)	1,5045	1,3882
(F---SO ₂ ---CHF---CO) ₂ O	119-120 (4)	1,8447	1,4102
F---SO ₂ ---CHF---CO---Cl	131-132	1,6159	1,3845
F---SO ₂ ---CHF---CO---OCH ₃	172,5	1,5060	1,3845
F---SO ₂ ---CHF---CO---OC ₂ H ₅	179-180	1,3959	1,3880

EXPERIMENTAL

Sulfofluoride monofluoroacetic acid. A quantity of 1.8 g of water was added dropwise with stirring and cooling (ice-salt mixture) to 16.2 g of α -hydrotrifluoroethane- β -sultone in a teflon reactor, the rate of addition being such that the reaction temperature did not exceed 5°. When all the water had been added, the reaction mass was heated gradually to 100° (in 1 hour); traces of hydrogen fluoride were removed by heating at 100° and a pressure of 40-50 mm. The crystalline residue (15.1 g) was almost pure sulfofluoride monofluoroacetic acid. To obtain the chemically pure compound, the technical product was recrystallized from 15 ml of chloroform. The yield was 14.4 g, which is 90% of theoretical. Found: C 15.26; H 1.45; F 24.00; S 19.81%; acidity equivalent 3.04. C₂H₂O₄F₂S. Calculated: C 15.00; H 1.25; F 23.73; S 20.00%; acidity equivalent 3.00.

Sulfofluoride monofluoroacetic acid (white prisms) is soluble in water, ether, benzene, and acetone. When kept in moist air it deliquesces, forming a viscous transparent liquid which distills under reduced pressure and is the dihydrate of sulfofluoride monofluoroacetic acid. The following equivalents were found: acidity 3.03, hydrolyzable fluorine 1.01, water 2.03.

Sulfofluoride monofluoroacetic anhydride. A mixture of 16.0 g of sulfofluoride monofluoroacetic acid and 10.6 g of phosphorus pentoxide (50% excess) was heated on a water bath for half an hour. By fractionation of the semi-liquid mixture we obtained 13.8 g of sulfofluoride monofluoroacetic anhydride (91% yield). Found: C 16.11; H 0.92; F 25.42; S 20.96%; acidity equivalent 6.12. $C_4H_2O_7F_4S_2$. Calculated: C 15.89; H 0.66; F 25.16; S 21.20%; acidity equivalent 6.00.

Acyl chloride of sulfofluoride monofluoroacetic acid. A mixture of 16.0 g of sulfofluoride monofluoroacetic acid and 23.0 g of phosphorus pentachloride was heated on a water bath for about a half hour, until a homogeneous mass was obtained. By fractionation we obtained 16.6 g of the acyl chloride of sulfofluoride monofluoroacetic acid (93% yield). Found: F 20.96; Cl 20.20%; mol. wt. 174.4; acidity equivalent 4.05. $C_2HO_3F_2ClS$. Calculated: F 21.28; Cl 19.90%; mol. wt. 178.6; acidity equivalent 4.00.

Methyl ester of sulfofluoride monofluoroacetic acid. To 17.8 g of the acyl chloride of sulfofluoride monofluoroacetic acid was added 3.2 g of ethanol; yield 93%. By fractionation we obtained 16.9 g of the methyl ester of sulfofluoride monofluoroacetic acid; yield 97%.

SUMMARY

1. Sulfofluoride monofluoroacetic acid was obtained by the controlled hydrolysis of α -hydrotrifluoroethane- β -sultone.
2. A number of derivatives of sulfofluoride monofluoroacetic acid were obtained.

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1. M. A. Dmitriev, G. A. Sokol'skii and I. L. Knunyants, *Izvestiya Akad. Nauk SSSR. Otd. Khim. Nauk* 1035 (1960).
2. M. A. Dmitriev, G. A. Sokol'skii and I. L. Knunyants, *Izvestiya Akad. Nauk SSSR. Otd. Khim. Nauk* 1227 (1960).

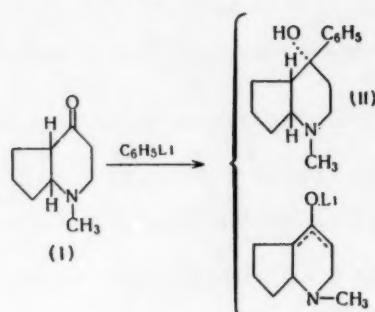
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SYNTHESIS AND SPATIAL CONFIGURATION OF CERTAIN 1-METHYL-4-PHENYL-4-PIPERIDOLS *

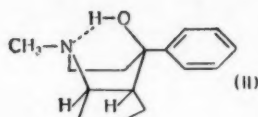
Z. A. Mistryukov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 4, pp. 623-626, April, 1961
Original article submitted January 1, 1960

In one of the previous reports the synthesis of certain 4-piperidones was described [1]. In the present investigation, by reacting these piperidones with phenyllithium we obtained the corresponding phenyl alcohols, the propionic esters of which may have an anesthetic effect. When 1-methyl-4-piperidone (I) was reacted with phenyllithium, only one isomer of 1-methyl-4-phenyl-4-piperidol (II) was obtained (~44% yield)

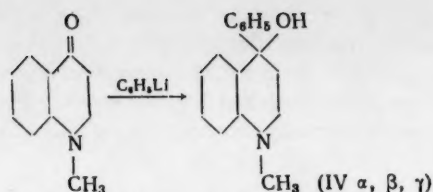


Attempts to separate the other possible isomers from the reaction mass were not successful. We only obtained considerable amounts of the initial amino ketone (I), formed as a result of the competing reaction heading to formation of an enol-metallic compound (I), together with small amounts of a diamine ($C_{16}H_{28}N_2$) and amino alcohol ($C_{23}H_{29}NO$), which were not investigated further. The infrared spectra of the phenyl alcohol (II) showed that it contained a clearly expressed intramolecular hydrogen bond. On the basis of this fact, we must assign a "boat" shape to the piperidine ring in the amino alcohol (II), because only this structure would allow sufficient proximity of the hydroxyl and amino group to form a hydrogen bond. For the same reason it must be assumed that the coupling of the rings in this isomer is evidently "cisoid", which is fairly obvious from an examination of the molecular models



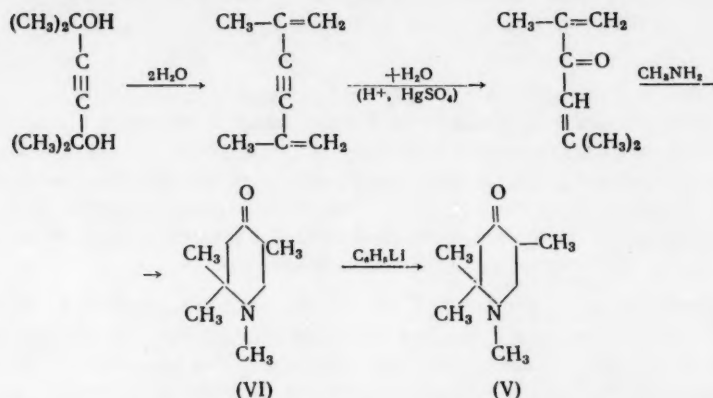
The nearest bicyclic analog of the above-examined ketone (I), 1-methyldecahydroquinolone-4 (III), behaves appreciably differently from (I) in the phenyllithium synthesis. When decahydroquinolone (III) was reacted with phenyllithium, of the four theoretically possible diastereoisomers we obtained three isomeric forms of 1-methyl-4-phenyldecahydroquinolol-4 (IV), (isomers α , β , and γ) with a total yield of 63.7%, the ratio of the isomers being 62% α , 24% β , and 14% γ . In this case the amount of unreacted amino ketone was appreciably less

* The present investigation was carried out under the direction of Academician I. N. Nazarov.

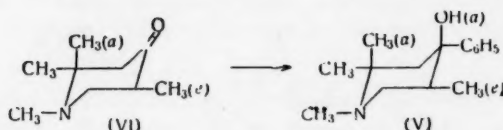


The spatial configuration of the isomeric amino alcohols (IV) obtained is now being investigated.

In addition to the above-mentioned amino alcohols (II) and (IV), 1,2,2,5-tetramethyl-4-phenyl-4-piperidol (V) was also synthesized, in the following way [2]:



Dehydration of tetramethyl butindiol gave a 57% yield of 2,5-dimethylhexadiene-1,5-diene-3; the yields given in the literature [3] were not obtained. The reaction of piperidone (VI) with phenyllithium gave only one isomer of amino alcohol (V) instead of the two theoretically possible isomers. From an examination of the spatial models it is seen that the most favorable structure for piperidone (VI) is the conversion form with the piperidine ring in the form of a "chair" and an equatorial methyl group at C (5), because with this configuration the interaction of the uncombined substituents would be minimum. With this location of the substituents, the carbonyl group in piperidone (VI) is strongly shielded by the methyl group at C (2), as a result of which, phenyllithium can approach only from the side opposite this group:



Therefore, the piperidol (V) obtained by the phenyllithium synthesis must have a configuration with an equatorial position of the phenyl group at C (4) and a methyl group at C (5). In contrast to phenyl alcohol (II), an investigation of the infrared spectra of alcohols (IV α , β , γ) did not show an appreciable tendency of the latter to form an intramolecular hydrogen bond; this confirms that their piperidine rings have a "chair" shape.

EXPERIMENTAL

1-Methyl-4-phenyl-4-piperidol (II). A solution of 1-methyl-4-piperidol [1] (127.6 g, 0.832 M) in 160 ml of ether was added in 1.5 hours to a solution of phenyllithium, prepared from 17 g (2.44 M) of lithium and 128 ml (1.22 M) of bromobenzene, in 400 ml of ether at -8 – -10° . The reaction mass was stirred for 30 minutes at -10° and was left overnight at room temperature; after it had been boiled for 4 hours, 500 ml of 5 N hydrochloric acid was added and the ether layer was removed. The base obtained from the aqueous solution by the action of NaOH (150 g) was extracted with ether. After the ether had been removed under vacuum the residue was distilled. The following fractions were collected: (i) a b.p. of 80 – 145° (1.5 mm); (ii) a b.p. of 146 – 175° (1.5 mm); weight 87.5 g and (iii)

a b.p. of 175-150° (1.5-2 mm); weight 7 g. From the first fraction, 26.4 g of the initial 1-methyl-4-piperidone (b.p. 55-57° at 0.5 mm; n_D^{20} 1.4955) was obtained after re-distillation. The second fraction was dissolved in 150 ml of dioxan and to it was added (with cooling) 95 ml of a 4.16 N solution of dry HCl in dioxan and 50 ml of acetone (for homogenization). The mixture was left to stand, and 78 g of 1-methyl-4-phenyl-4-piperidol (II) hydrochloride was deposited; m.p. 221-222° (from methanol-ethyl acetate). Found: Cl 13.24%. $C_{15}H_{22}NOCl$. Calculated: Cl 13.20%.

The base obtained from this hydrochloride had a b.p. of 136-146° (0.3 mm), and an m.p. of 45.5-46.5° (from petroleum ether). The picrate had an m.p. of 157-157.5° (from propyl alcohol). Found: C 54.72; H 5.35; N 12.51%. $C_{21}H_{24}N_4O_8$. Calculated: C 54.80; H 5.22; N 12.25%.

The third fraction was dissolved in benzene and filtered through Al_2O_3 . After part of the benzene had been evaporated, isooctane was added to the residue. When the mixture was allowed to stand, 1.5 g of the crystalline base, with an m.p. of 71-72°, was obtained. Found: C 82.15; H 8.54; N 4.03%. $C_{23}H_{28}NO$. Calculated: C 82.30; H 8.66; N 4.18%.

After the hydrochloride of the phenyl alcohol (II) had been separated, the mother liquors were evaporated and the base was obtained from the residue by means of NaOH; the picrate of the base was obtained (in CH_3COOH). Together with considerable amounts of 1-methyl-4-phenyl-4-piperidol (II) picrate, fractional crystallization of the picrates from acetic acid gave ~5.5 g of a new picrate with an m.p. of 199-200° (with decomposition). From this picrate we obtained 2.7 g of base with an m.p. of 48-50° (from hexane); the m.p. of the propionate hydrochloride was 206-207° (from ethyl acetate-methanol). From its analysis, the propionate corresponded to the composition $C_{19}H_{22}N_2Cl$. The structure of the two latter products was not investigated.

1-Methyl-4-phenyldecahydro-4-quinolol (IV). 1-Methyldecahydroquinolone-4 (47.8 g, 0.287 M) in 50 ml of ether was added (with cooling by ice) in a 1 hour to a solution of phenyllithium, prepared from 5.9 g of lithium and 45.5 ml of bromobenzene, in 200 ml of ether. After the reaction mass had been boiled for 3 hours, 180 ml of 5 N HCl was added with cooling by ice, the ether layer was separated, and the base was precipitated from the aqueous layer by solid NaOH. The base was extracted with chloroform, the solvent was evaporated and by fractional crystallization of the residue from isooctane and toluene we obtained the following individual isomers of 1-methyl-4-phenyldecahydro-4-quinolol (IV): (i) 27.3 g of the α -isomer with an m.p. of 126.5-127° (from dichloroethane). Found: C 78.71; H 9.51; N 6.17%. $C_{16}H_{23}NO$. Calculated: C 78.37; H 9.38; N 5.72%; (ii) 11 g of the β -isomer with an m.p. of 112-113° (from isooctane). Found: C 78.59; H 9.67; N 5.50%. $C_{16}H_{23}NO$. Calculated: C 78.37; H 9.38; N 5.72%; the hydrochloride of the β -isomer melted at 216-219° (from ethyl acetate-methanol); (iii) 6.5 g of the γ -isomer with an m.p. of 148-150° (from dichloroethane). Found: C 78.23; H 9.44; N 5.90%. $C_{16}H_{23}NO$. Calculated: C 78.37; H 9.38; N 5.72%.

During crystallization, the β -isomer attracts considerable amounts of the α -isomer; its final purification was therefore carried out chromatographically on Al_2O_3 or by crystallization of the hydrochloride from a mixture of ethyl acetate and methanol.

2,5-Dimethylhexadiene-1,5-ine-3 [4]. A well-ground mixture of 71 g of tetramethyl butindiol, 7.1 g of para-toluenesulfonic acid and 0.1 g of pyrogallol was placed in a distillation flask and heated at 100° (100-120 mm). Distillation of the water and hydrocarbon was completed in one hour. The hydrocarbon layer was separated, dried with $MgSO_4$ and distilled. We obtained 30.1 g of 2,5-dimethylhexadiene-1,5-ine-3 (b.p. 46-49° at 40 mm) and 8.6 g of 2,5-dimethylhexene-5-ine-3-ol-2 (b.p. 64-67° at 13 mm) [5].

1,2,2,5-Tetramethyl-4-piperidone-4 (VI). A quantity of 49 g of a mixture of 2,5-dimethylhexadiene-1,4-one-3 and the corresponding methoxy ketones [4] was mixed with 50 ml of 38% aqueous methylamine. In 5 minutes, homogenization took place with liberation of heat, and the solution was left to stand for two days at 20°. For hydrolysis of the imine impurity and separation from the neutral products, the solution was acidified with 71 ml of concentrated HCl, heated for 10 minutes at 100°, cooled and extracted with ether. The base was precipitated from the solution with solid NaOH, extracted with ether, dried with K_2CO_3 and distilled. We obtained 38 g of base with a b.p. of 91-102° (15 mm). Re-distillation of this fraction gave an over-all 40% yield of pure 1,2,2,5-tetramethyl-4-piperidone (VI); the b.p. was 90-93° (15 mm); n_D^{20} 1.4620. Found: C 69.89; H 10.70; N 9.65%. $C_9H_{16}ON$. Calculated: C 69.82; H 10.33; N 9.04%. The hydrochloride melted at 195.5° (from $n-C_4H_9OH$), the picrate melted at 180-180.5° (from alcohol).

1,2,2,5-Tetramethyl-4-phenyl-4-piperidol (V). A solution of 88.8 g of 1,2,2,5-tetramethylpiperidone-4 (0.57 M) in 80 ml of ether was added (with cooling by ice) in 1.5 hours to a solution of phenyl lithium, prepared from 12.1 g

of lithium (1.74 M) and 136.6 g of bromobenzene (0.87 M), in 500 ml of ether. The reaction mass was boiled for 3 hours, left overnight and treated with 160 ml of concentrated HCl in 300 ml of water; a considerable amount of piperidol (V) hydrochloride hydrate was precipitated. The crystals were filtered and washed with ether; the filtrate was extracted with ether and added to the crystals. A quantity of 250 ml of ether was added to this mixture and the base was precipitated with 100 g of solid NaOH. After the evaporation of the ethereal extract, the following fractions were collected by distillation of the residue: (I) b.p. up to 135° (3 mm), weight 16.3 g; (II) b.p. 135-143° (3 mm), weight 11.9 g; (III) b.p. 143-170° (3 mm), weight 80.3 g. Fractions (II) and (III) crystallized when mixed with isooctane. After filtration and drying under vacuum, 67.8 g of 1,2,2,5-tetramethyl-4-phenyl-4-piperidol (m.p. 81-82°) was obtained. Found: C 77.58; H 9.55; N 6.64%. $C_{16}H_{23}NO$. Calculated: C 77.40; H 9.45; N 6.02%.

The hydrochloride of this amino alcohol melted at 201° (from acetone-chloroform). The hydrochloride crystallized from water in the form of the hydrate (m.p. 152-153°).

SUMMARY

The synthesis of certain 1-methyl-4-phenyl-4-piperidols is described and suggestions are made regarding their possible spatial configuration.

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STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

COMMUNICATION 4. ESTERIFICATION REACTION AND STEREOCHEMIC STRUCTURE OF CERTAIN 4-PHENYL-4-PIPERIDOLS

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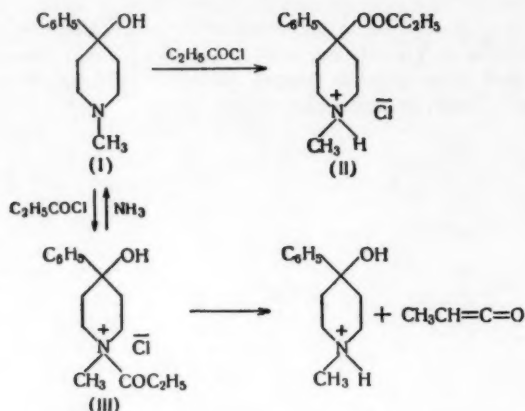
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 4, pp. 627-632, April, 1961

Original article submitted January 12, 1960

It is known that acyl chlorides of acids react with alcohols particularly vigorously in the presence of tertiary amines, the acylating agent in this case being the complex of the amine and acyl chlorides [1]. The presence of tertiary amino group and hydroxyl in the molecule of N-alkyl-4-phenyl-4-piperidols makes it possible to assume that their esterification by acid acyl chlorides may also take place in this general system, as a result of intermolecular acylation. If this is true, in the case of geometric isomers of different N-methyl-4-phenyl-4-piperidol compounds such a reaction may serve as one of the methods for determining their configuration. The present report deals with the investigation of this problem.

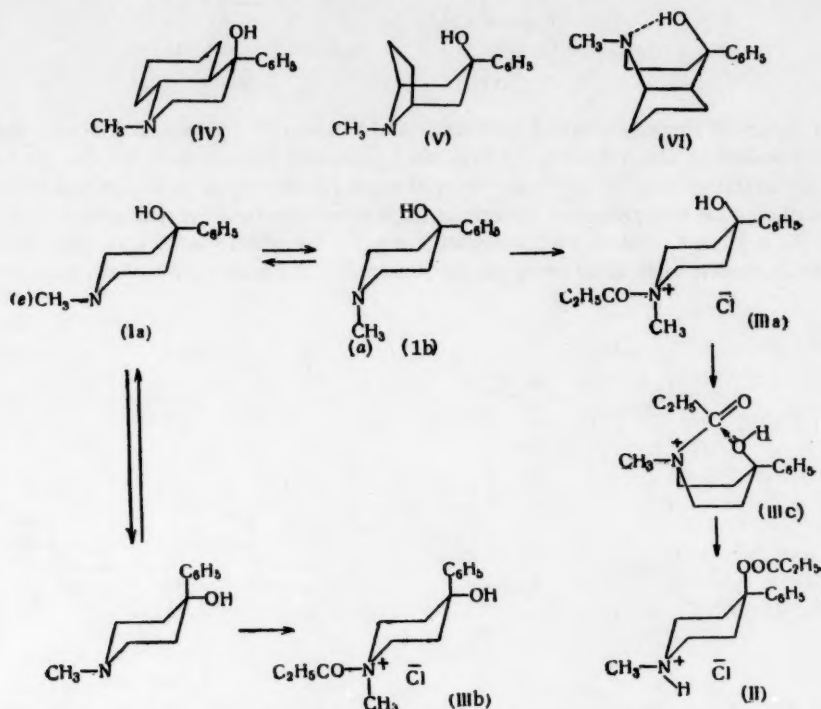
When propionates of N-alkyl-4-phenyl-4-piperidol (I) were obtained from bases of amino alcohols and propionyl chloride, it was found that piperidols (I) may be divided into two distinct groups with respect to this reagent. The first group of these amino alcohols forms hydrochlorides of the propionic esters (II) extremely readily; the alcohols of the second group give fairly stable quaternary complexes with the acylating agent, giving the initial base with ammonia or alkalis, or the corresponding hydrochlorides



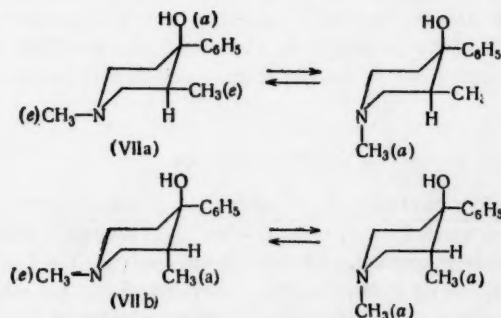
The hydrochlorides of the bases of amino alcohols (I) are evidently formed by the decomposition of quaternary complexes of type (III) [2]. From these data it may be assumed that for alcohols of the first group the amine and hydroxyl groups are either adjacent to each other or there is the possibility of such proximity, and that, in consequence, this esterification reaction may serve as confirmation of their configuration. In point of fact, 1-methyl-4-phenyl trans-decahydro-4-quinolol (IV) [3], in which the functional groups cannot be adjacent as a result of rigid trans-linking of the rings, does not give the corresponding ester when acted on by propionyl chloride. 3-Phenyl 3-tropinol (V), in which the hydroxyl group is located in the cis-position to the ethylene bridge [5], behaves similarly. In contrast, 1-methyl-4-phenyl-4-piperidol (VI), in which—as was previously shown [3]—the amine and hydroxyl functions are adjacent, esterifies very readily. Here, it must be noted that for amino alcohols (I) the

formation of two types of complexes with propionyl chloride may be visualized, with *cis*- and *trans*-location of the hydroxyl and acyl groups (IIIa) and (IIIb). For amino alcohols (IV) and (V), it is equally impossible for either the *cis*- or *trans*-complex to give an ester, as a result of the rigidity of the ring, which prevents the approach of the reacting groups.

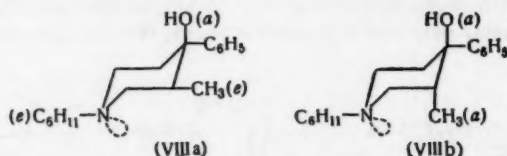
Complexes of monocyclic amino alcohols (I) may regroup into an ester only in the case of the *cis*-position of the acyl and hydroxyl groups, because only then is it possible for the reacting groups to converge with conversion of



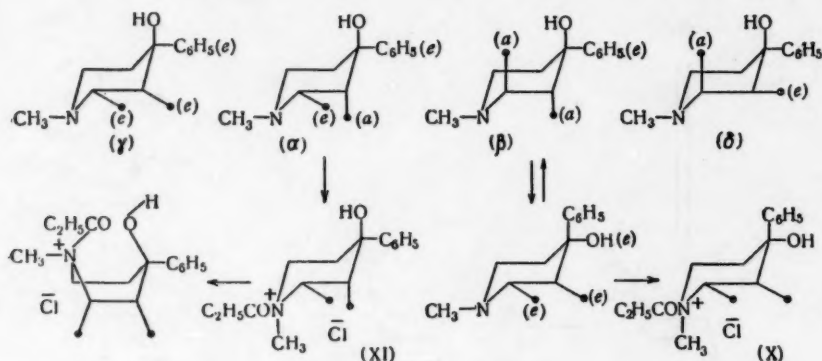
the ring into a "boat" (IIIa-IIIc). As a result of the comparatively large volume of the propionyl group compared with that of the methyl group, and because of the easy conversion of the methyl group from the equatorial to an axial position (as a result of the proximity of the volumes of the free electron pair of nitrogen and methyl [6]), the complexes most readily formed are those with an equatorial acyl group; therefore it may be assumed that amino alcohols with an axial hydroxyl group will be the most readily esterified. The esterification of 1-alkyl-3-methyl-4-phenylpiperidin-4-ol may serve as an illustration of this assumption. If the alkyl group at the nitrogen is a methyl one [7], then, as a result of the large volume of phenyl, both isomers of the amino alcohol (VIIa) and (VIIb) will differ from each other only by the position of the methyl at C (3), i.e., with propionyl chloride both isomers will give complexes [with *cis*-location of the acyl and hydroxyl group (type IIIa)], which can readily undergo regrouping into an ester



In point of fact, both isomers (VIIa and VIIb) readily form esters with propionyl chloride. But if conversion at the nitrogen is hindered by replacement of the methyl group by a heavier radical, for example, a cyclohexyl radical (VIII), we may expect the formation of a complex with propionyl chloride, in which the heavier cyclohexyl group will be equatorial, while the acyl group will be axial, i.e., with a trans-orientation with respect to hydroxyl



In actual fact, with propionyl chloride both isomers of 3-methyl-1-cyclohexyl-4-phenyl-4-piperidol (VIIIa) and (VIIIb) give complexes from which the original bases are regenerated by a solution of soda. We made attempts to employ the above-examined theories of the acylation of N-substituted-4-phenyl-4-piperidol compounds for determining the configuration of the four geometric isomers of 1,2,3-trimethyl-4-phenyl-4-piperidol (IX α , β , γ , δ) [8]. It was found that only the α -isomer could be readily acylated, whereas the others readily give good yields of the hydrochlorides of propionic esters when acted on by propionyl chloride. An examination of the most probable stable



configurations of these isomers shows that compounds (β) and (α) may be included in the difficultly acylated amino alcohols. Amino alcohol (β) may be included in the difficultly acylated compounds in the case where the configuration reacts with an axial phenol group, which gives a complex of type (IIIb) with a trans-located acyl and hydroxyl group (X). Although amino alcohol (α) must give a complex with a cis-location of the reacting groups (XI), conversion of such a complex to the "boat" form may, however, be disadvantageous as a result of the reaction of the two cis-methyl groups with each other and with the hydrogens at C (5) and C (6). Therefore, on the basis of acylation data there are two possible structures for a difficultly acylated alcohol - β or α . The final choice between these two structures will be possible when certain additional data is employed. The esters of the above-indicated difficultly acylated amino alcohols were obtained by the methods given under EXPERIMENTAL.

The hydrochlorides of the propionic esters synthesized in this way were tested for their analgesic activity in the S. Ordzhonikidze All-Union Chemico-Pharmaceutic Scientific-Research Institute by Professor Mashkovskii. The hydrochlorides of the propionates of amino alcohols (IV) and (IX β and δ) were inactive, those of amino alcohols (IX α) and (VI) had an activity close to that of morphine, while the hydrochloride of the propionate of the γ -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol had an activity more than 30 times greater (on mice) than the activity of morphine.

EXPERIMENTAL

Preparation of the hydrochlorides of propionates of amino alcohols under mild conditions. Esterification of readily acylated amino alcohols was carried out by gradual addition of propionyl chloride to a solution of the amino alcohol in dichloroethane, chloroform or acetone, with stirring and cooling. The hydrochloride of the propionic ester sometimes crystallized immediately, while at other times, a seed crystal or ether was added. The typical procedure will be described by way of the example of 1,2,3-trimethyl-4-phenyl-4-piperidol.

Hydrochloride of the propionate of the β -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol. Propionyl chloride (6 ml) was added with stirring and cooling to a suspension of 6.43 g of the β -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol [8] in 15 ml of dichloroethane. The amino alcohol dissolved rapidly with liberation of heat. Crystallization took place when the mass was cooled. The crystals were filtered, washed with ether and dried under vacuum. We obtained 8.9 g of the hydrochloride of the propionate of the β -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol (m.p. 236°). An analytical sample was prepared by crystallization from dichloroethane; m.p. 236-236.5°. Found: N 4.53; Cl 11.40%. $C_{17}H_{26}NO_2Cl$. Calculated: N 4.50; Cl 11.40%.

Hydrochloride of the propionate of the γ -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol. From 6.43 g of the γ -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol [8] in 15 ml of dichloroethane and 10 ml of propionyl chloride we obtained 9.29 g of the unpurified hydrochloride; crystallization of the latter from a mixture of dichloroethane and dioxan gave 7.36 g of the pure hydrochloride of the propionate of the γ -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol (m.p. 181-181.5°). Found: N 4.47; Cl 11.28%. $C_{17}H_{26}NO_2Cl$. Calculated: N 4.50; Cl 11.40%.

Hydrochloride of the propionate of 1-methyl-4-phenyl-4-piperidol. We obtained 4.51 g of unpurified ester hydrochloride (m.p. 172-173°) from 4.18 g of 1-methyl-4-phenyl-4-piperidol [3] (0.0181 M) in 3 ml of chloroform and 1.75 ml of propionyl chloride (0.02 M). After recrystallization from a mixture of ethyl acetate and methanol we obtained pure 1-methyl-4-phenyl-4-piperidol propionate hydrochloride (m.p. 173.5-174.5°). Found: C 66.70; H 8.14; N 4.49; Cl 11.14%. $C_{18}H_{26}NO_2Cl$. Calculated: C 66.80; H 8.05; N 4.33; Cl 11.01%.

The action of propionyl chloride on difficultly acylated amino alcohols under mild conditions. The initial bases were obtained by the action of propionyl chloride on the amino alcohols of a difficultly acylated group under the above-indicated conditions, followed by treatment of the reaction mixture with dilute NH_3 or Na_2CO_3 . Typical examples are given below. Propionyl chloride (7 ml) was added gradually (with cooling by ice) to a suspension of 3.05 g of the α -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol [8] in 5 ml of chloroform. The amino alcohol dissolved rapidly with appreciable liberation of heat. The solution obtained was left for 20 min at 20°, the solvent was removed under vacuum, the residue was dissolved in water, treated with excess dilute ammonia and extracted with chloroform. We obtained 2.5 g of the initial amino alcohol (identified by the melting point) from the chloroform extract after crystallization from isooctane. By a similar method, from 0.51 g of the α -isomer of 3-methyl-1-cyclohexyl-4-phenyl-4-piperidol (m.p. 141°) in 2.5 ml of dichloroethane and 0.33 ml of propionyl chloride (2 molar equivalents) after 3 hours at 20° and subsequent treatment as above (using a solution of Na_2CO_3 instead of dilute NH_3) we obtained - after recrystallization from heptane - 0.3 g of the initial base. Under similar conditions we obtained 0.7 g of the initial amino alcohol from 1.13 g of the β -isomer of 3-methyl-1-cyclohexyl-4-phenyl-4-piperidol (m.p. 101-102°). Amino alcohols (IV) and (V) react with propionyl chloride in a similar way.

The Action of Propionyl Chloride on Difficultly Acylated Amino Alcohols Under Severe Conditions

Hydrochloride of the propionate of the α -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol. Propionyl chloride (4 ml) was added gradually to a suspension of 2.41 g of the α -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol [8] in 4 ml of propionic anhydride. The amino alcohol dissolved rapidly with liberation of heat. The solution obtained was heated at 96-98° for 12 hours; the excess reagents were removed under vacuum with heating to 100° and the residue was dissolved in ethyl acetate. With careful addition of ether, crystallization took place. The crystals were filtered, washed with ethyl acetate and dried under vacuum; we obtained 2.48 g of unpurified ester hydrochloride (m.p. 169-172°). After recrystallization from a mixture of ethyl acetate and methanol, 1.94 g of the hydrochloride of the propionate of the α -isomer of 1,2,3-trimethyl-4-phenyl-4-piperidol (m.p. 168-177° with decomposition) was obtained. Found: C 65.23; H 8.39; N 4.47; Cl 11.41%. $C_{17}H_{26}NO_2Cl$. Calculated: C 65.48; H 8.36; N 4.50; Cl 11.40%.

Hydrochloride of the propionate of the α -isomer of 1-methyl-4-phenyldecahydro-4-quinolol. We obtained 1.98 g of the propionate hydrochloride of the α -isomer of 1-methyl-4-phenyldecahydro-4-quinolol (m.p. 228-229°) from 2.56 g of the α -isomer of 1-methyl-4-phenyldecahydro-4-quinolol [3] in 4 ml of propionic anhydride. Found: C 67.60; H 8.45; N 3.98; Cl 10.58%. $C_{19}H_{28}NO_2Cl$. Calculated: C 67.50; H 8.28; N 4.14; Cl 10.51%.

Under these conditions 3-phenyl-3-tripionol [4] was not esterified. With longer heating, the dehydration product was obtained.

SUMMARY

1. It was shown that the esterification reaction of bases of N-alkyl-4-phenyl-4-piperidol compounds by propionyl chloride can be used for determining their configuration.

2. A number of 4-phenyl-4-piperidol-4 propionates were obtained.

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SYNTHESIS AND TRANSFORMATIONS OF UNSATURATED CARBOXYLIC ACIDS

COMMUNICATION 2. A NEW METHOD OF SYNTHESIZING UNSATURATED γ -KETO ACIDS

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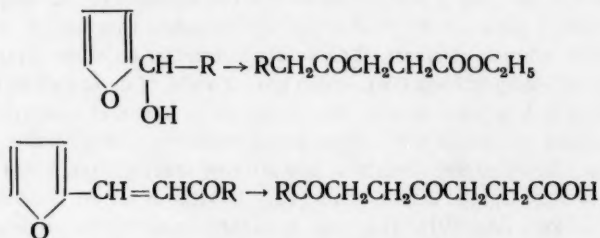
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Original article submitted February 25, 1960

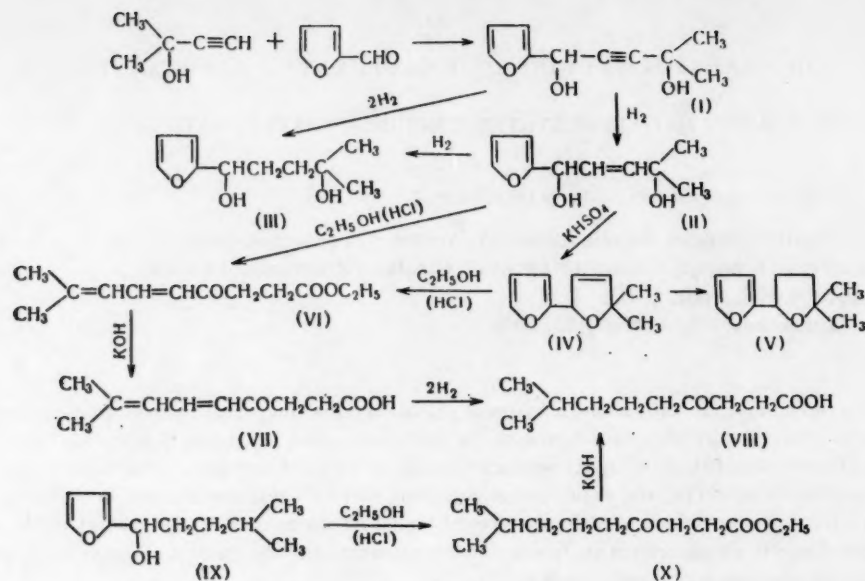
As a result of numerous investigations it has been established that long-chain unsaturated carboxylic acids are an essential part of several very important liquids of the animal organism [1], lipids of microbic cells [2], and of several classes of antibiotics [3]. The higher unsaturated acids and their functional derivatives are especially interesting as factors in vitamin action [4] and as substances possessing very valuable and interesting physiological properties [5, 6]. A search for a synthetic route to different types of higher unsaturated acids [7] is therefore of considerable interest, and the objective of the present study was the development of a new method of preparing γ -keto acids containing a system of conjugated double bonds.

It was shown previously that suitable starting materials for the synthesis of saturated γ -keto acids are found in various alkylfuryl-carbinols [8] and furfurylidene ketones [9], the opening of the furan ring which enables the carbon chain to be lengthened at once by five carbon atoms with good yields.



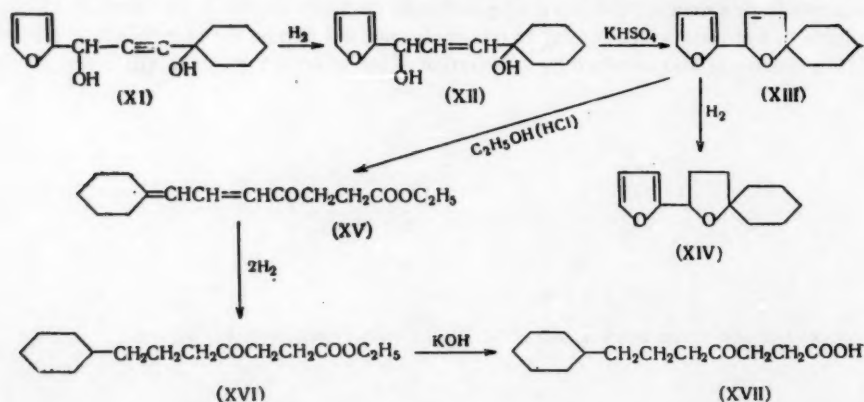
For the purpose of synthesizing unsaturated γ -keto acids we studied in detail the transformations of the acetylenic γ -glycol (I), which was prepared by reacting furfural with a Mg-organic derivative of dimethylethinylcarbinol [10]. It was found that the acetylenic glycol (I) could be selectively hydrogenated with Pd/CaCO₃ to the corresponding ethylenic γ -glycol (II), which could be hydrogenated further to the saturated γ -glycol (III). As its structure suggests, the ethylenic glycol (II) can be readily dehydrated, and when it was heated with potassium bisulfate it gave a 70% yield of 2,2-dimethyl-5-furyl-2,5-dihydrofuran (IV). The ultraviolet spectrum of the dihydrofuran derivative (IV) showed the presence of a double bond not conjugated with the furan ring [11]. By catalytic hydrogenation with a Pd catalyst one mole of hydrogen added readily to this compound and formed the corresponding 2,2-dimethyl-5-furyl-tetrahydrofuran (V), which was also obtained by dehydration of the saturated γ -glycol (III).

*For Communication 1 of this series see *Izv. AN SSSR, Otd. Khim. Nauk*, 1512 (1960).



The furylacetylenic γ -glycol (I) was found to be very sensitive to the action of alcoholic hydrogen chloride under conditions necessary to open the furan ring [12], and for this reason a mixture of products together with a large quantity of tar was obtained in the transformation. However, the opening of the furan ring of the ethylenic glycol (II) is an easier reaction, and in this case a yield of up to 25% was obtained of the ethyl ester of 4-keto-8-methylnonadien-5,7-oic acid (VI), which gave a good yield of the corresponding unsaturated γ -keto acid (VII) when it was saponified with a water-alcohol solution of alkali. The acidic isomerization of the furan ring was much better in the case of 2,2-dimethyl-5-furyl-2,5-dihydrofuran (IV), which gave a yield of up to 65% of the diene γ -keto ester (VI) when it was boiled for one hour in a solution of ethyl alcohol in the presence of catalytic quantities of hydrogen chloride. The ester (VI) absorbed two moles of hydrogen during catalytic hydrogenation, but it did not give an adduct with maleic anhydride, and according to the ultraviolet and infrared spectra (Figs. 1 and 2) it contained a keto group conjugated with a system of two conjugated double bonds [13]. In view of all this evidence there was not much doubt about the structure of the diene keto ester (VI). However, in order to confirm the presence in it of the γ -keto group a counter synthesis was carried out in which 4-keto-8-methylnonanoic acid (VIII) was formed by hydrogenation of the diene keto acid (VII). With the same end in view isomylfurylcarbinol (IX) [14] was converted into the γ -keto ester (X), saponification of which resulted in the desired γ -keto acid (VIII), which did not give a depression with the sample prepared above.

We also used the above scheme for synthesizing diene γ -keto acids in the case of furylacetylenic γ -glycol (XI) obtained by reacting furfural with the Mg-organic derivatives of cyclohexylethynylcarbinol. This



glycol, like the γ -glycol (I) described above, could be selectively hydrogenated over Pd/CaCO_3 in a solution of aqueous methanol to form the ethylenic glycol (XII), which was converted without being isolated into the corresponding derivative of dihydrofuran (XIII). This product contained a double bond not conjugated with the furan ring, and it added on one mole of hydrogen to form 2-furyloxa-1-spirodecane (XIV), which was also prepared by dehydrating the product obtained by adding two moles of hydrogen to the original γ -glycol (XI). Under conditions of acidic isomerization in a solution of ethyl alcohol the furan ring of the dihydrofuran (XIII) readily opened and gave the diene γ -keto ester (XV) in a yield of up to 50%, the infrared spectrum of which was found to be completely identical with that of the ester of 4-keto-8-methylnonadien-5,7-oic acid (VI) described above. When the unsaturated γ -keto ester (XV) was hydrogenated catalytically it added on two moles of hydrogen, and was converted into the saturated γ -keto ester (XVI), saponification of which gave 7-cyclohexyl-4-ketoheptanoic acid (XVII).

This method which we have developed for preparing unsaturated γ -keto acids is quite simple and convenient, and at the present time we are studying in detail the possibility of using it for synthesizing various unsaturated γ -keto acids is quite simple and convenient, and at the present time we are studying in detail the possibility of using it for synthesizing various unsaturated γ -keto acids with long and branched chains.

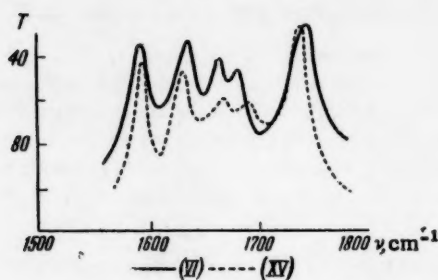


Fig. 1.

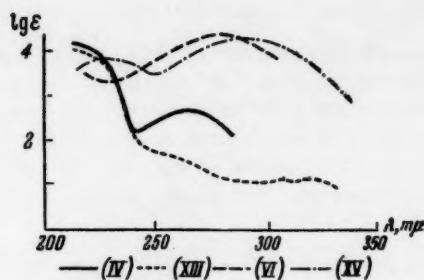


Fig. 2.

EXPERIMENTAL

Acetylenic γ -glycol (I). A solution of magnesium ethyl bromide was prepared from 24.3 g of Mg and 121 g of ethyl bromide in 250 ml of ether, and to it was added slowly (during one and one half hours) at a temperature not above 8° , a solution of 42 g of dimethylethynylcarbinol in 50 ml of benzene, after which the mixture was stirred at this temperature for one more hour. The ether was distilled off and was replaced by benzene after which the magnesium addition compound was reacted with a solution of 48 g of furfural in 50 ml of benzene which was added over the course of two hours while stirring vigorously at a temperature of -2 to $+2^\circ$. The mixture was then kept at $12-15^\circ$ for two hours and decomposed with a saturated solution of ammonium chloride at $4-6^\circ$. The benzene layer was separated, the aqueous portion was carefully extracted with ether, and the combined benzene-ether solution was dried over potash. The solvent was distilled off, and the crystalline reaction product was carefully washed on a filter with petroleum ether. The yield of the acetylenic γ -glycol (I) was 53.6 g (60%), and after it was crystallized from a 1:1 mixture of ether and petroleum ether it melted at $59.5-60.5^\circ$. Found: C 66.32; 66.24; H 6.83; 6.92%. $\text{C}_{10}\text{H}_{10}\text{O}_3$. Calculated: C 66.65; H 6.71%.

Hydrogenation of the acetylenic γ -glycol (I). A solution of 15 g of the acetylenic γ -glycol (I) in a mixture of 40 ml of methanol and 5 ml of water was hydrogenated over Pd/CaCO_3 . After one mole of hydrogen had been absorbed the rate of hydrogenation decreased markedly and hydrogenation was discontinued. The catalyst was filtered off, and the solvent was distilled off under vacuum. Yield was 12.8 g (84.7%) of the ethylenic γ -glycol (II) with b.p. $103-104^\circ$ (0.3 mm); n_D^{20} 1.5081. Found: C 65.76; 65.57; H 7.81; 7.80%. $\text{C}_{10}\text{H}_{14}\text{O}_3$. Calculated: C 65.91; H 7.74%.

Exhaustive hydrogenation of the acetylenic γ -glycol (I) over Pd/CaCO_3 resulted in the absorption of two moles of hydrogen, and after distillation a 69% yield was obtained of the saturated glycol (III), with b.p. $111-113^\circ$ (0.37 mm); n_D^{20} 1.4952. Found: C 64.84; 65.00; H 8.69; 8.62. $\text{C}_{10}\text{H}_{16}\text{O}_3$. Calculated: C 65.19; H 8.75%.

Dehydration of the ethylenic γ -glycol (II). A solution of 4.5 g of the ethylenic γ -glycol (II) in 40 ml of benzene was added drop by drop to 0.45 g of finely ground KHSO_4 heated to 120° with simultaneous distillation under vacuum (50 mm). The distilled mixture of water, benzene, and dehydration product was dried with potash, the benzene was

distilled off, and the residue was distilled under vacuum. Yield of dihydrofuran derivative (IV) was 2.7 g (66.7%) with b.p. 72-73° (8 mm); n_D^{20} 1.4802; λ_{\max} 216 m μ 10200. Found: C 72.80; H 7.30%. $C_{10}H_{12}O_2$. Calculated: C 73.14; H 7.37%.

When (IV) was catalytically hydrogenated over Pd/CaCO₃ in a solution of methanol one mole of hydrogen was absorbed, and after distillation a quantitative yield was obtained of 2,2-dimethyl-5-furyltetrahydrofuran (V) with b.p. 78-79° (8 mm); n_D^{20} 1.4747; Found: C 72.31; 72.16; H 8.27; 8.43%. $C_{10}H_{14}O_2$. Calculated: C 72.26; H 8.49%.

4-Keto-8-methylnonadien-5,7-oic acid (VII) and its ethyl ester (VI). To a solution of 4.4 g of (IV) in 50 ml of absolute ethyl alcohol was added 0.3 ml of a saturated alcoholic solution of hydrogen chloride, and the mixture was boiled for one hour. The alcohol was distilled off under vacuum, and the residue was treated with water and neutralized with sodium bicarbonate; the reaction product was extracted with ether and dried with magnesium sulfate. After the solvent was distilled off distillation of the residue under vacuum gave 3.4 g (60.4%) of the diene γ -keto ester (VI) with b.p. 98-99° (0.25 mm); n_D^{20} 1.5196. λ_{\max} 235.5 m μ ; $\lg \epsilon$ 3.26; $\lambda_{\max} = 279$ m μ ; $\lg \epsilon$ 4.412. The infrared spectrum had characteristic absorption bands at 1591, 1633, 1677, and 1738 cm⁻¹. Found: C 68.44; 68.21; H 8.70; 8.64%. $C_{12}H_{18}O_3$. Calculated: C 68.54; H 8.63%.

The 2,4-dinitrophenylhydrazone of the diene γ -keto ester (VI) melted at 137-138° (alcohol). Preparation of the same γ -keto ester from the ethylenic γ -glycol (II) using the method described above gave a yield of only 22.5%.

Saponification was carried out by boiling a mixture of 1.5 g of the unsaturated γ -keto ester (VI), 10 ml of methanol, 1 ml of water, and 0.5 g of potassium hydroxide for one hour; the alcohol was distilled off under vacuum, 10 ml of water was added to the residue, the neutral products were extracted with ether, and the aqueous layer was acidified with 20% sulfuric acid; the saponified product was extracted with ether and dried with magnesium sulfate. After the ether was distilled off the yield was 1.09 g (84%) of 4-keto-8-methylnonadien-5,7-oic acid (VII) with m.p. 97-5-98.5° (from petroleum ether). Found: C 66.30; 66.00; H 7.97; 7.89%. $C_{10}H_{14}O_3$. Calculated: C 65.91; H 7.74%.

When the acid (VII) was hydrogenated with Pd/CaCO₃ two moles of hydrogen was absorbed and a quantitative yield was obtained of 4-keto-8-methylnonanoic acid (VIII) with m.p. 61.9-62.5° (from hexane). Found: C 64.42; 64.64; H 9.67; 9.85%. $C_{10}H_{18}O_3$. Calculated: C 64.49; H 9.74%.

Isoamylfurylcarbinol (IX) and its transformation. Furfural and magnesium i-amyl bromide were reacted using the method of [14], and a yield of 86.5% of i-amylfurylcarbinol (IX) was obtained with b.p. 110-111° (12 mm); n_D^{20} 1.4700.

i-Amylfurylcarbinol (IX) was isomerized by adding 0.5 ml of an alcoholic solution of hydrogen chloride to a solution containing 19 g of (IX) in 120 ml of absolute ethyl alcohol and boiling the mixture for one hour. After the usual treatment and distillation under vacuum we obtained;

a) 5 g of product with b.p. 106.5-107° (21 mm); n_D^{20} 1.4514 which according to its analysis corresponded to the ethyl ether of i-amylfurylcarbinol. Found: C 73.45; 73.66; H 10.20; 10.08%. $C_{12}H_{20}O_2$. Calculated: C 73.43; H 10.27%.

b) 10.1 g (41.5%) of the ethyl ester of 4-keto-8-methylnonanoic acid (X) with b.p. 130-131° (6 mm); n_D^{20} 1.4374, which was saponified to the corresponding γ -keto acid (VIII) with m.p. 61-62°, and which did not give a depression with the sample described above.

Acetylenic γ -glycol (XI) and its transformations. Furfural and cyclohexylethynylcarbinol when reacted according to the method described above gave a yield of 87% of the acetylenic γ -glycol (XI) with m.p. 89.5-90° (from hexane). Found: C 71.23; 71.26; H 7.48; 7.42%. $C_{13}H_{16}O_3$. Calculated: C 70.90; H 7.32%. When it was hydrogenated over Pd/CaCO₃ in an aqueous methanol solution, one mole of hydrogen was selectively absorbed, after which the hydrogenation slowed down markedly. The ethylenic γ -glycol (XII) in a viscous high-boiling liquid which can be readily dehydrated by heating it to 100°. Dehydration was carried out by adding a solution of 61 g of the unsaturated ethylenic γ -glycol (XII) in 250 ml of benzene slowly (over two hours) to anhydrous KHSO₄ heated to 120° with simultaneous vacuum distillation (50 mm). The azeotropic mixture of benzene and water was distilled off, and the residue was distilled under vacuum. 36 g (65%) of the dehydration product (XIII) was obtained with b.p. 70-71° (0.22 mm); n_D^{20} 1.5105; λ_{\max} 217 m μ ; ϵ 10650. Found: C 76.46; 76.20; H 8.24; 7.90%. $C_{13}H_{16}O_2$. Calculated: C 76.44 H 7.90%.

When the dihydrofuran derivative (XIII) was hydrogenated over Pd/CaCO₃ one mole of hydrogen was absorbed and a good yield was obtained of 2-furyloxa-1-spirodecane (XIV) with b.p. 65-66° (0.09 mm); n_D^{20} 1.5062. Found: C 75.96; H 8.70. C₁₃H₁₈O₂. Calculated: C 75.69; H 8.80%.

Ethyl ester of the γ -keto acid (XV) and its transformations. An alcoholic solution of the dihydrofuran (XIII) was boiled in the presence of hydrogen chloride following the method described above and a yield of 46% was obtained of the diene γ -keto ester (XV) with b.p. 132-133° (0.08 mm); n_D^{20} 1.5308; λ_{\max} 231 m μ ; $\lg \epsilon$ 3.835; λ_{\max} 292.5 m μ ; $\lg \epsilon$ 4.270. The infrared spectrum had characteristic absorption bands at 1592, 1632, 1685, and 1734 cm⁻¹. Found C 72.35; 72.15; H 8.50; 8.69%. C₁₅H₂₂O₃. Calculated: C 71.97; H 8.86%.

When the ester (XV) was catalytically hydrogenated it absorbed two moles of hydrogen and after distillation a quantitative yield was obtained of the saturated γ -keto ester (XVI) with b.p. 121-122° (0.22 mm); n_D^{20} 1.4638. Found: C 70.91; 71.04; H 10.31; 10.10%. C₁₅H₂₆O₃. Calculated: C 70.83; H 10.30%. Saponification with a water-alcohol solution of alkali resulted in a 90% yield of 4-keto-7-cyclohexylheptanoic acid (XVII) with m.p. 65-65.5° (from hexane). Found: C 69.19; 69.10; H 9.92; 9.79%. C₁₃H₂₂O₃. Calculated: C 68.99; H 9.80%.

SUMMARY

A new method was developed for synthesizing diene γ -keto acids and their esters based on available furyl-acetylenic γ -glycols.

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DEMETHYLATION AND ISOMERIZATION OF PSEUDOCUMENE ON ALUMINOSILCATES

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The dealkylation of alkylaromatic hydrocarbons and the transfer of their alkyl groups have been studied in the work of a number of investigators. The earliest investigations in this field, which dealt with reactions conducted in the presence of aluminum chloride, had the principal purpose of developing a process for the production of toluene

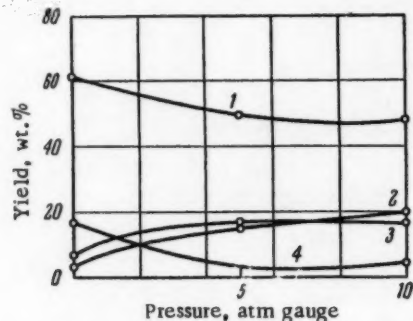


Fig. 1. Dependence of the yield of aromatic hydrocarbons on the pressure in the conversion of a mixture of benzene with pseudocumene: 1) Benzene; 2) toluene; 3) xylenes; 4) trimethylbenzenes.

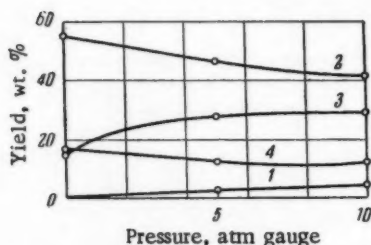


Fig. 2. Dependence of the yield of aromatic hydrocarbons on the pressure in the conversion of a mixture of toluene with pseudocumene: 1) Benzene; 2) toluene; 3) xylenes; 4) trimethylbenzenes.

[1-3]. In a number of investigations synthetic aluminosilicates were used successfully in dealkylations and alkylations [4-6]. In earlier work published by us results were reported of investigations on the transfer of methyl groups, isomerization of o- and m-xylenes, and demethylation of these xylenes in the presence of benzene [7, 8]. It was found that increasing of the pressure to 10-15 atm had a favorable effect on the dealkylation and conjugated alkylation of aromatic hydrocarbons. Application of vacuum suppressed the transfer of methyl groups and had the effect of directing the reaction in such a manner that a conversion which amounted for all practical purposes to a selective isomerization of the initial xylene resulted. Isomerization of m-xylene was also investigated in work done by other authors [9, 10].

With the development of a number of present-day branches of production based on petrochemical synthesis, xylenes acquired great importance from the practical standpoint. These hydrocarbons, as has been demonstrated by the results of published work [11, 12], can be produced by converting products of coke-chemical and pyrolysis industrial processes. Products resulting from the processes mentioned were subjected to conversion at temperatures of 450-500° and pressures of 5-10 atm, using aluminosilicates as catalysts. The polymethylbenzenes contained in these products were dealkylated and conjugated alkylation of toluene took place with the formation of considerable quantities of xylenes.

With a view of investigating the reactions taking place in the course of this complex process, a number of experiments on the catalytic conversion of individual aromatic hydrocarbons and mixtures of these hydrocarbons was carried out. The present work reports results obtained in the investigation of the catalytic conversion of pseudocumene, benzene, toluene, and mixtures of these hydrocarbons in the presence of synthetic aluminosilicates.

EXPERIMENTAL

As the initial products pseudocumene, benzene, and toluene were used. The pseudocumene originated from the Khar'kov Coke-

TABLE 1. Characteristics of Products of the Catalytic Conversion of Mixtures of Pseudocumene with Benzene and of Pseudocumene with Toluene (effect of the pressure) (Temperature 480°; volume velocity 0.5 hrs⁻¹)

Fractional composition and characteristics of product	Mixture of pseudocumene with benzene 1:2	Pressure			Mixture of pseudocumene with toluene 1:2	Pressure		
		atmos-pheric	5 atm	10 atm		atmos-pheric	5 atm	10 atm
Beginning of boiling, °C	80	79,5	74,5	75,0	103,7	82,5	75,5	75,0
Beginning of boiling, °C	—	Yield of fraction, weight percent			—	—	—	—
boiling	66,42	60,45	48,98	47,56	—	—	—	—
83-88	—	0,5	0,10	0,40	—	—	—	—
88-103	—	0,52	0,87	1,43	—	—	—	—
103-108	—	0,66	0,73	0,63	0,32	0,48	0,84	0,56
108-113	—	3,80	15,18	20,45	66,66	0,70	1,2	3,08
113-118	—	0,29	0,64	0,10	0,14	0,26	0,42	0,47
118-125	—	0,44	0,82	0,28	0,12	0,75	0,26	1,32
125-136	0,14	1,08	0,70	0,88	0,25	55,15	0,75	1,44
136-144	—	6,61	16,62	16,47	0,15	46,97	46,97	41,46
144-149	—	0,74	1,64	0,64	0,07	0,52	0,36	—
149-160	—	1,52	1,69	0,74	0,44	0,51	0,51	0,95
160-165	—	1,94	0,68	0,71	0,41	1,61	0,78	—
165-175	30,91	17,46	3,36	4,46	28,66	15,09	28,0	29,30
End of boiling, °C	—	0,94	—	—	—	0,87	0,63	0,59
175-End of boiling, °C	—	181,5	166	167,5	167,5	1,16	0,83	1,23
Total yield, wt. %	169	96,95	92,27	94,87	97,22	2,42	96,05	93,70
Iodine number	97,47	2,64	4,42	3,01	1,96	2,63	3,42	2,92
Residue, wt. %	1,6	0,41	3,31	2,12	1,82	1,01	0,53	3,38
Losses, wt. %	0,93	—	—	—	—	1,4997	1,4991	1,5000
n _D ²⁰	1,5018	1,5010	1,5009	1,5008	1,4998	—	—	—
d ₄ ²⁰	0,8742	0,8745	0,8748	0,8743	0,8676	0,8666	0,8674	0,8690
Degree of sulfonation, % by volume	100	100	100	100	100	100	100	100
Iodine number	1,2	3,4	2,3	0,9	0,52	3,6	3,0	2,2
Material balance, wt. %	—	98,2	93,8	91,72	—	98,6	93,8	89,3
Catalyzate	—	—	0,95	1,3	—	—	1,6	2,9
Gas	—	—	1,2	4,3	—	—	1,7	5,1
Coke	—	0,8	4,05	5,68	—	0,4	2,9	2,7
Losses	—	1,0	—	—	—	1,0	—	—

TABLE 2. Characteristics of the Principal Aromatic Fractions

Characteristics of the fraction	Mixture of pseudocumene with benzene 1:2	Pressure			Mixture of pseudocumene with toluene, 1:1	Pressure		
		atmospheric	5 atm	10 atm		atmospheric	5 atm	10 atm
Fraction 78—83°								
Yield, wt. %	66,42	60,45	48,98	47,56	—	—	1,2	3,08
n_D^{20}	1,5012	1,5011	1,5012	1,5011	—	—	1,4995	1,4990
d_4^{20}	0,8786	0,8790	0,8775	0,8780	—	—	—	0,8745
Bromine number	0	0,07	0,032	0,064	—	—	—	0
Fraction 108—113°								
Yield, wt. %	—	3,8	15,18	20,45	66,66	55,15	46,97	41,46
n_D^{20}	—	1,4978	1,4977	1,4978	1,4970	1,4971	1,4971	1,4970
d_4^{20}	—	0,8670	0,8643	0,8645	0,8660	0,8650	0,8655	0,8658
Bromine number	—	0	0,032	0,032	0	<0,04	<0,04	<0,04
Fraction 136—144°								
Yield, wt. %	—	6,61	16,62	16,47	—	15,09	28,0	29,3
n_D^{20}	—	1,4995	1,4993	1,4989	—	1,4986	1,4990	1,4986
d_4^{20}	—	0,8675	0,8676	0,8678	—	0,8648	0,8650	0,8662
Bromine number	—	—	0,1	0,04	—	<0,04	<0,04	<0,04
Fraction 165—175°								
Yield, wt. %	30,91	17,46	3,36	4,46	28,66	16,96	12,95	11,42
n_D^{20}	1,5053	1,5052	1,5049	1,5042	1,5049	1,5044	1,5044	1,5048
d_4^{20}	0,8760	0,8744	0,8738	0,8755	0,8753	0,8735	0,8745	0,8770

Chemical Plant. It boiled within the range of 167-168.5°; d_4^{20} 0.8751; n_D^{20} 1.5049. The benzene was of the cryoscopic grade: boiling range 78-80°; d_4^{20} 0.8720; n_D^{20} 1.5012; bromine number less than 0.01; degree of sulfonation 100%. The toluene had a boiling range of 109.9-111.0°; d_4^{20} 0.8669; n_D^{20} 1.49, 70 (sic) [6]; iodine number zero; degree of sulfonation 100%.

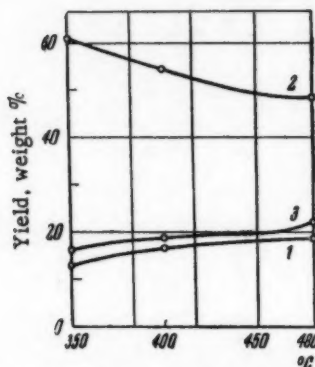


Fig. 3. Dependence of the yield of aromatic hydrocarbons on the temperature applied in the conversion of pseudocumene: 1) Xylenes; 2) trimethylbenzenes; 3) tetramethylbenzenes.

well as characteristics of the aromatic fractions. Curves showing the relation of the yields of benzene, toluene, xylenes, and trimethylbenzenes to the pressure can be seen in figures 1 and 2.

As catalysts synthetic aluminosilicates produced by the Baku and Grozny Catalyst Plants were used. Experiments involving application of high pressures were conducted at a laboratory installation of the continuous flow type. The experiments conducted at atmospheric pressure and in vacuum were carried out in a reactor in which a fluidized solid layer of microspheric aluminosilicate catalyst was employed. The equipment in question was described in the articles [12-13].

Dealkylation of pseudocumene and conjugated alkylation of benzene and toluene. Mixtures of pseudocumene and benzene and pseudocumene and toluene were subjected to catalytic conversion.

The weight ratio of the initial components in the original mixture amounted to 1 : 2. At the temperature of 480° and a volume velocity of 0.5 hrs⁻¹, a number of experiments were carried out at different pressures. The analyses of the initial mixtures and of the resulting catalyzates are listed in Tables 1 and 2 as

TABLE 3. Characteristics of Products of the Catalytic Conversion of Pseudocumene on Aluminosilicate (effect of the temperature) (Pressure = 1 atm; volume velocity, 0.5 hrs⁻¹)

Fractional composition and characteristic of products	480°	450°	400°	350°
Beginning of boiling °C	103	109	122	133,5
Yield of fraction, wt. %				
B. p. —113	}	}	}	}
113—118				
118—125	}	}	}	}
125—136				
136—144	18,52	18,0	16,64	13,36
144—149	1,05	0,50	1,04	1,02
149—160	2,16	1,86	1,90	2,0
160—165	1,74	2,80	2,62	2,34
165—175	48,57	49,52	54,28	60,89
175—185	1,88	1,64	0,98	1,25
Distillation end point	185	185	185	185
Total yield, wt. %	76,50	78,28	79,32	81,35
Residue, wt. %	22,49	19,56	18,96	16,35
Losses, wt. %	1,01	2,16	0,82	2,30
n _D ²⁰	1,5063	1,5061	1,5061	1,5058
d ₄ ²⁰	0,8768	0,8761	0,8772	0,8764
Degree of sulfonation, % by vol.	100	100	100	100
Material balance, wt. %	94,5	95,0	97,4	97,5
Catalyzate	1,9	1,9	1,4	1,4
Coke	2,3	2,0	Losses	—
Gas	1,3	1,1	1,2	1,1

TABLE 4. Characteristics of the Principal Aromatic Fractions

Characteristics of fraction	480°	450°	400°	350°
Fraction 136—144°				
Yield, % by weight	18,52	18,0	16,64	13,26
n _D ²⁰	1,4990	1,4988	1,4983	1,4993
d ₄ ²⁰	0,8654	0,8660	0,8659	0,8666
Iodine number	0,53	0	0	0
Fraction 165—175°				
Yield, % by weight	48,57	49,52	54,28	60,89
n _D ²⁰	1,5042	1,5042	1,5040	1,5046
d ₄ ²⁰	0,8732	0,8731	0,8711	0,8734
Iodine number	1,2	—	2,0	1,8

At atmospheric pressure there was dealkylation of pseudocumene to a minor extent and conjugated alkylation of benzene under formation of 3.8% of toluene and of approximately 7% of a mixture of xylenes. Under these conditions there was practically no dismutation of pseudocumene and no formation of tetramethylbenzenes was detected. At 5 atm an almost complete conversion of pseudocumene was achieved. The content of toluene and xylenes in the catalyzate comprised 15.2 and 17%, respectively. The yield of gaseous products amounted to 0.9%; that of coke to 1.2%. The conversions characteristic for the process were dealkylation of pseudocumene and conjugated alkylation of benzene. Increasing of the pressure to 10 atm increased the extent of the conversions mentioned in the sense that the content of toluene in the catalyzate rose to 20.5% and that of xylenes dropped to 16.5%. The yield of gaseous products of the reaction yield increased to some extent and became equal to 1.3%.

TABLE 5. Characteristics of Products of the Catalytic Conversion of Pseudocumene (effect of vacuum) (Temperature 480°; volume velocity 0.5 hrs⁻¹)

Fractional composition and characteristics of products	Pressure mm. Hg				
	760	350	100	50	100*
Beginning of boiling °C	103	112,5	133	131	142
Yield or fractions, weight percent					
B. p. -113	}	0,29	—	—	—
113-118		0,13	—	—	—
118-125		0,41	—	—	—
125-136		0,33	0,64	0,82	—
136-144	}	18,52	14,53	7,55	} 1,74
144-149		1,05	0,56	0,88	
149-160		2,16	2,07	1,50	
160-165		1,74	2,73	2,91	
165-175		48,57	55,31	71,27	89,22
175-185		1,88	1,79	1,53	2,16
Distillation endpoint		185	185	185	185
Total yield, wt. %		76,50	87,00	86,11	96,96
Residue, wt. %		22,49	11,64	12,01	2,82
Losses, wt. %		1,01	1,36	1,88	0,22
n _D ²⁰		1,5063	1,5059	1,5052	1,5052
d ₄ ²⁰		0,8768	0,8765	0,8754	0,8758
Degree of sulfonation, % by vol.	100	100	100	100	100
Material balance, wt. %					
Catalyzate		94,5	97,80	97,4	97,80
Coke		1,9	0,55	0,6	0,87
Gas		2,3			
Losses		1,3	1,65	2,0	1,33

* Temperature 350°.

TABLE 6. Characteristics of Aromatic Fractions

Characteristics of fractions	Pressure, mm Hg				
	760	350	100	50	100 *
Fraction 136 - 144°					
Yield, wt. %	18,52	14,53	6,80	7,55	1,74
n _D ²⁰	1,4990	1,4988	1,4992	1,4993	1,4993
d ₄ ²⁰	0,8654	0,8660	0,8665	0,8668	—
Iodine number	0,53	1,33	1,9	2,0	—
Fraction 165 - 175°					
Yield, wt. %	48,57	55,31	72,12	71,27	89,22
n _D ²⁰	1,5042	1,5045	1,5043	1,5047	1,5049
d ₄ ²⁰	0,8732	0,8739	0,8745	0,8736	0,8735
Iodine number	1,2	1,4	0,9	1,9	1,8

* Temperature 350°.

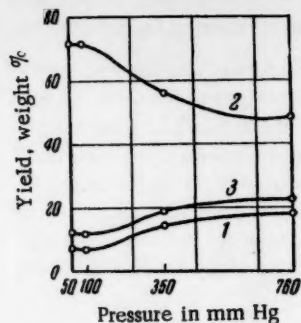
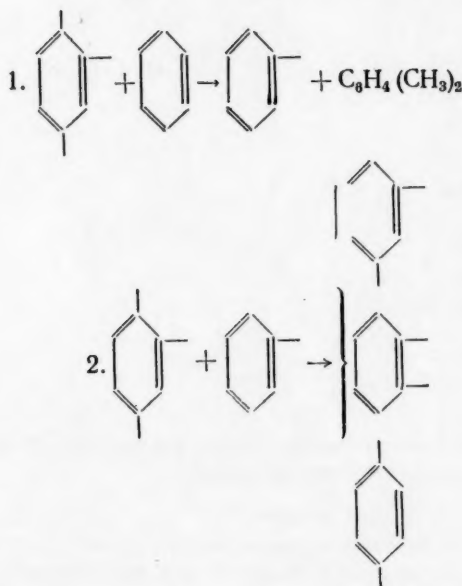


Fig. 4. Dependence of the yield of aromatic hydrocarbons on the pressure applied in the conversion of pseudocumene: 1) Xylenes; 2) trimethylbenzenes; 3) tetramethylbenzenes.

pseudocumene to a major extent, so that the following principal reactions became predominant in the process:



Transfer of methyl groups and isomerization of pseudocumene. A number of experiments on the catalytic conversion of pseudocumene were carried out. The effects of the temperature and pressure were investigated. The results of analyses of the products obtained at different temperatures have been systematically arranged and listed in Tables 3 and 4. The curves expressing the relation between the yields of the principal aromatic fraction and the temperature and pressure are given in figures 3 and 4.

At 480° the degree of conversion of pseudocumene amounted to 50%. Dismutation of the pseudocumene took place with the formation of 19% of xylenes and 22% of tetramethylbenzenes. Lowering of the temperature to 450° did not bring about any significant change in the fractional composition of the product. Further lowering of the temperature reduced the extent of transfer of alkyl groups. For instance, at 400° the yield of xylenes comprised 17% and that of tetramethylbenzenes 19% in relation to the catalyzate. Isomerization of the initial pseudo-

The catalyzates had a low content of unsaturated hydrocarbons: their iodine number varied within the range of 1-3. The catalytic conversion of a mixture of pseudocumene and toluene (Table 1, Fig. 2) also exhibited the characteristic traits of dealkylation and alkylation of the initial hydrocarbons. At atmospheric pressure the yield of the xylene fraction comprised 15% of the catalyzate. An increase of the pressure increased the extent of the reactions mentioned: at pressures in the range of 5-10 atm the yield of the xylene fraction reached 28-30%. This fraction, on the basis of the results obtained in spectroscopic analysis, contained approximately 25% of p-xylene, 55% of m-xylene and 20% of o-xylene. A further increase of the pressure contributed to hydrogenating cracking of the methyl groups of the alkylaromatic hydrocarbons with the result that a certain quantity of benzene and of gaseous products was formed.

The presence of an aromatic component (benzene or toluene) in the mixture suppressed the dismutation of

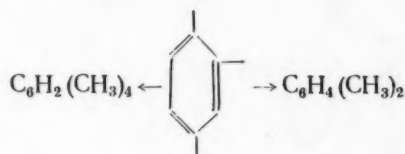
cumene took place. A spectroscopic investigation of the fraction of the catalyzate boiling at 165-175° indicated that approximately 20% of mesitylene and 5% of hemimellitene were present in it in addition to the pseudocumene.

With the purpose of suppressing dismutation and leading the process in the direction of the isomerization of pseudocumene, a number of experiments were conducted in vacuum. Results of the analysis of the products obtained are listed in Tables 5 and 6. At a residual pressure of 350 mm the yields of the xylene and tetramethylbenzene fractions comprised 14.5 and 19.9%, respectively. At a pressure of 100 mm the principal reaction that took place was isomerization of pseudocumene. The trimethylbenzene fraction consisted of 75-78% of pseudocumene, 17-20% of mesitylene, and 5-6% of hemimellitene. The content of the xylene and tetramethylbenzene fractions in the catalyzate decreased to 7 and 11.5%, respectively. A further decrease of the pressure down to 50 mm did not exert a significant effect on the course of the reaction: the composition of the product obtained did not differ from that obtained in the preceding experiment.

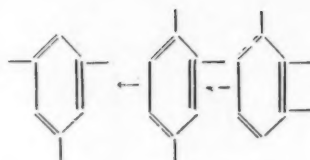
In vacuum (at a pressure reduced to 100 mm) lowering of the temperature to 350° suppressed completely the transfer of methyl groups. The content of xylenes dropped to 1.7% and that of tetraalkylbenzenes to 2.8%. In addition to that there was a reduction of the isomerization of pseudocumene and the product obtained had a relatively low content of mesitylene and hemimellitene.

Thus, at temperature of 450-480° the catalytic conversion of pseudocumene on aluminosilicates is characterized by the following principal reactions:

1. Transfer of methyl groups (dismutation of pseudocumene)



2. Isomerization of pseudocumene



Application of pressure enhanced disproportionation by the rearrangement of the methyl groups in pseudocumene whereas the use of vacuum suppressed this disproportionation.

SUMMARY

1. The dealkylation of pseudocumene accompanied by the conjugated alkylation of benzene and toluene was investigated at different temperatures and pressures in the presence of aluminosilicates.
2. Application of pressures in the range of 5-10 atm at temperatures of 450-480° expedited the reactions mentioned above. As a result of a single treatment of a mixture of pseudocumene with toluene, a yield of xylenes comprising approximately 30% of the catalyzate was obtained.
3. In the absence of benzene and toluene, pseudocumene was subjected to dismutation with the formation of a mixture of isomeric xylenes and tetramethylbenzenes.
4. Application of vacuum suppressed to a considerable extent the transfer of methyl groups and had the effect of channeling the reaction in the direction of the isomerization of pseudocumene.

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CATALYTIC SYNTHESIS OF NITRILES

COMMUNICATION IV. CYANATION OF ALLYL ALCOHOL

WITH AMMONIA

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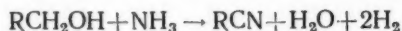
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The catalytic synthesis of acrylonitrile has been accomplished in various ways; among the most widely known methods is the addition of hydrogen cyanide to acetylene at 60-80° in the presence of an acidic aqueous solution of copper cyanide and ammonium, potassium or sodium chloride [1]. The Nieuwland catalyst of similar composition has also been used. The yield of nitrile reached 94%. Acrylonitrile has also been obtained by dehydration of ethylene cyanhydrin [2] in the presence of molten sodium acetate, or of ammonium acrylate [3] in the presence of a dehydrating catalyst at elevated temperatures.

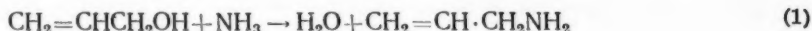
In our previous paper [4] it was shown that saturated alcohols react with ammonia on a nickel-alumina catalyst at 270-330° to give nitriles in yields of up to 95%. In the present work we have investigated the reaction between allyl alcohol and ammonia under similar conditions. However the experiments showed that propionitrile was obtained and not the expected acrylonitrile. The following combinations of oxides and of oxides and metals were therefore studied as catalysts.

1. Al_2O_3 (90 %), Fe_2O_3 (10 %);
2. Al_2O_3 (50 %), ZnO (50 %);
3. Al_2O_3 (85 %), Ni (10 %), Ag (5 %);
4. Al_2O_3 (85 %), Cu (15 %)
5. Al_2O_3 (96,5 %), ZrO_2 (3,5 %);
6. TiO_2 (95 %), Al_2O_3 (5 %);
7. TiO_2 (90 %), ZnO (10 %)

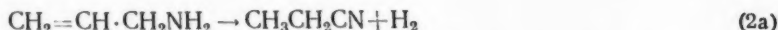
Experiments at different temperatures were carried out with each of these catalysts. However in all cases the reaction proceeded with the formation of propionitrile and a mixture of propylamines. These results appear unexpected only at a first glance. In fact one should take into account the fact that the catalytic cyanation of alcohols with ammonia occurs in a reducing medium; not only water but two molecules of hydrogen are removed.



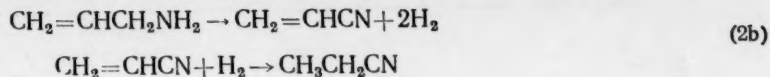
The reaction evidently goes in the following two steps:



The unsaturated amine produced in the conditions discussed is either converted into propionitrile on the catalyst by rearrangement of the hydrogens in the adsorption complex

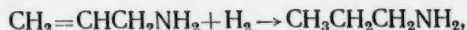


or it undergoes dehydrogenation into acrylonitrile which is reduced to propionitrile before being desorbed

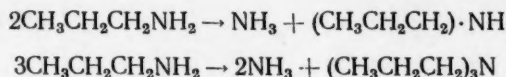


Schemes (2a) and (2b) are so similar that the experimental data obtained are insufficient for one to be preferred to the other.

There is no doubt that the propylamines formed as by-products are produced by hydrogenation of allylamines formed in the first stage of the reaction



and the propylamine is in part transformed further into di- and tri-propylamines.



EXPERIMENTAL

The method of preparing the nickel-alumina catalyst has been described by us previously [4]. Other catalysts based on alumina were prepared by careful mixing of the requisite metal oxides. The catalyst containing nickel and silver (3) was made by impregnating alumina with the metal nitrates. The alumina was dried, heated until nitrogen dioxide was evolved, and reduced with hydrogen at 390°. The copper-alumina catalyst (5) was prepared by reduction with hydrogen at 280° of copper oxide deposited on activated alumina. In all experiments the apparent volume of catalyst was 65 ml, and the length of the layer from 40 to 45 cm.

The allyl alcohol used in the experiments boiled at 96-97° (748 mm) and had d_4^{20} 0.8549; n_D^{20} 1.4135. The literature data for this alcohol are: b.p. 97.06° (760 mm); d_4^{20} 0.86911 [5]; d_4^{20} 0.8540; n_D^{20} 1.41345 [6].

Each experiment lasted 30 min. However experiments lasting several hours were carried out as a control on the stability of the catalyst and to obtain sufficient catalyzate to determine the nature of its constituents. The results obtained are cited in the table. As one can see from the data cited the greatest quantity of nitrile nitrogen, up to 23.1%, was detected in the catalyzate obtained at 330° using a nickel-alumina catalyst containing 30% nickel. 23.0 g of this catalyzate, obtained in some repeat experiments, was studied. The amine was separated by extraction with dilute hydrochloric acid. The residue, which contained the alcohol and nitrile, was dried with potash and distilled at 749 mm. The following were obtained; fraction I, b.p. 78-93°, 1.1 g; fraction II, b.p. 93-96°; 16.2 g; d_4^{20} 0.7861; n_D^{20} 1.3685; residue 1.4 g. Fraction II consisted mainly of propionitrile, for which the following constants appear in the literature: b.p. 95.0-95.2° (722 mm) [7]; d_4^{20} 0.7862; n_D^{20} 1.3681 [8]. The fraction contained 99.7% propionitrile. On hydrolysis it gave an acid with b.p. 140-141°; its anilide melted at 103°. Amines (2.9 g) were separated from the acid extract. The amines were a mixture of n-propyl-, dipropyl-, and tripropylamines with a preponderance of the last. These results show that when allyl alcohol is cyanated on a nickel-alumina catalyst the product is not acrylonitrile propionitrile and a mixture of propylamines. Similar results were obtained with other nickel-alumina catalysts containing less nickel.

A catalyzate containing 15.9% nitrile nitrogen was obtained at 480° in the presence of mixed iron oxide, aluminum oxide catalyst. From 16.0 g of combined catalyzate obtained under these conditions, 6.9 g of a nitrile was separated; it had b.p. 94-96° (754 mm); d_4^{20} 0.7860; n_D^{20} 1.3685. On hydrolysis it gave propionic acid, b.p. 139-141° (756 mm); its anilide melted at 103°. Thus allyl alcohol and ammonia form propionitrile in the presence of an iron oxide/aluminum oxide catalyst.

On investigating 31.0 g of a catalyzate obtained at 450° in the presence of a catalyst of equal parts of aluminum and zinc oxides, 14.4 g of propionitrile was separated: b.p. 93-95° (756 mm); d_4^{20} 0.7861 and n_D^{20} 1.3685. The anilide of the acid obtained by hydrolyzing this fraction had m.p. 103°. Apart from the nitrile a mixture of amines boiling from 144-156° was obtained. In the literature the boiling points of dipropyl- and tripropylamines are respectively 109.4-110.4° and 156° [9]. The nitrogen content of these amines, calculated from their formulas,

Catalytic Cyanation of Allyl Alcohol

Expt. No.	Temp., °C	Catalyst	Quantity of reactants, g		Catalyzate obtained, g		Content of nitrile nitrogen, %
			alcohol	NH ₃	total	dry	
1	300	30% Ni in Al ₂ O ₃	6,5	3,0	5,7	3,0	21,9
2	330	Same	6,5	3,2	5,6	2,9	23,1
3	360	»	6,5	2,9	4,1	2,3	17,6
4	270	15% Ni in Al ₂ O ₃	6,5	3,0	5,8	3,7	19,7
5	300	Same	6,5	3,0	5,8	3,5	21,3
6	330	»	6,5	3,0	5,8	3,3	18,5
7	270	7,5% Ni in Al ₂ O ₃	6,5	2,8	5,7	3,3	21,9
8	300	Same	6,5	2,8	6,1	3,7	21,3
9	330	»	6,5	2,8	5,8	3,3	15,2
10	450	Al ₂ O ₃ 90%, Fe ₂ O ₃ 10%	6,5	3,2	7,0	2,9	14,1
11	480	Same	6,5	3,2	4,8	1,9	15,9
12	390	Al ₂ O ₃ 50%, ZnO 50%	6,5	3,0	7,2	4,3	10,5
13	420	Same	6,5	3,0	6,5	4,0	12,9
14	450	»	6,5	3,0	6,4	3,8	14,3
15	300	Al ₂ O ₃ 85%, Ni 10%, Ag 5%	6,5	3,0	5,5	4,5	4,8
16	270	Al ₂ O ₃ 85%, Cu 15%	6,5	3,0	4,7	4,0	3,5
17	330	Al ₂ O ₃ 96,5%, ZrO ₂ 3,5%	6,5	3,0	6,2	2,9	3,0
18	390	TiO ₂ 90%, ZnO 10%	6,5	3,0	7,0	6,8	1,4
19	390	TiO ₂ 95%, Al ₂ O ₃ 5%	6,5	3,2	7,0	6,8	0,4

are for C₆H₁₅N 13.85% and for C₉H₂₁N 9.77%. On the basis of these data it can be concluded that in this case the catalyzate consisted of propionitrile and a mixture of dipropyl- and tripropylamines. An investigation of the catalyzate from the cyanation of allyl alcohol in the presence of a catalyst containing nickel and silver on activated alumina showed that in this case also propionitrile was formed. In view of their small content of nitrile nitrogen, the catalyzates from other experiments were only investigated qualitatively. Here too, propionitrile was observed.

SUMMARY

1. The cyanation of allyl alcohol with ammonia at temperatures from 270° to 480° and in the presence of various catalysts has been studied.
2. In all cases the reaction proceeded with the formation of propionitrile and a certain amount of a mixture of propylamines.
3. Ideas on the mechanism of the conversion of allyl alcohol into propionitrile on the catalyst surface have been discussed.

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THE CATALYTIC AMINATION OF ALCOHOLS

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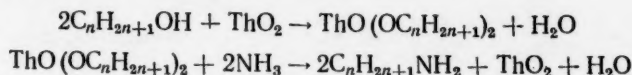
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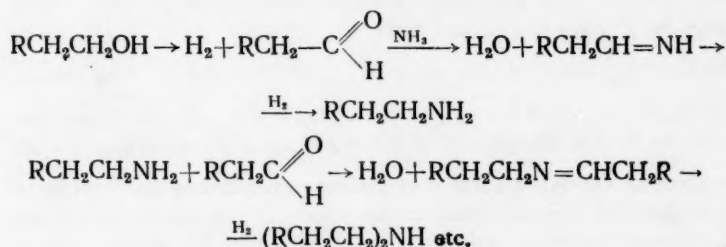
From our previous work [1, 2] and the investigations of other authors [3-7] it was evident that when alcohols are aminated on oxide catalysts the products included unsaturated and saturated hydrocarbons, hydrogen, aldehydes, ethers, nitriles, and water, in addition to the amines. The literature data on how these substances arise is very contradictory and does not permit correct conclusions to be drawn about the reaction mechanism, and the choice of catalyst and the reaction conditions.

Sabatier and Mailhe [4], starting from data on the amination of alcohols on thorium, suggested that the alcohol initially reacted with the catalyst to form an unstable ester, for example an alkyl thorate, which then rapidly reacted with ammonia to form a primary amine which does not eliminate olefins. Therefore unsaturated hydrocarbons appear among the amination products only as by-products:



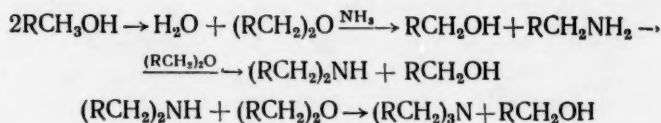
The primary amine in its turn reacts with alkyl thorate to give secondary and then tertiary amines.

Schwegler and Adkins [5] showed that aldehydes and ketones appeared among the amination products as intermediate products resulting from dehydrogenation of the alcohols. These (carbonyl compounds) react with ammonia initially to give imines which are then reduced by hydrogen to primary amines. The latter react further with fresh aldehyde molecules to give secondary and then tertiary amines.

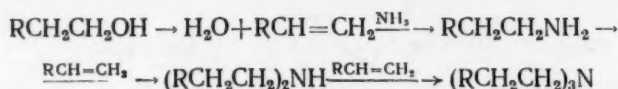


This scheme excludes the possibility of forming amines from tertiary alcohols because the latter cannot be converted into aldehydes or ketones.

Baum [6] studied the catalytic amination of primary aliphatic alcohols and came to the conclusion that the amines are obtained by the reaction of ammonia with simple ethers, which are formed from the alcohols as intermediate substances:

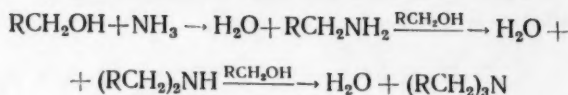


Popov [7] on the basis of his own experiments concluded that initially dehydration of the alcohols to alkenes occurred under the influence of the dehydrating part of the catalyst. The alkenes then react with ammonia to form a primary amine, and the latter subsequently gives secondary and tertiary amines:



Later Popov and Shuikin [8] carried out a more careful study of the replacement of hydroxyl groups by amino-groups and came to the conclusion that amines were formed by simultaneous elimination of the elements of water from a molecule of alcohol and one of ammonia or from alcohol and an amine as they lie side by side on the catalyst surface.

Since the suggestions in each of the cited papers is of interest for a correct judgement on the mechanism of amination of alcohols, we decided to return to the problem. To this end we carried out experiments on the amination under standard conditions of butanol-1, a mixture of butene, butyraldehyde, and also pentene-1, octene-1, and di-isoamyl ether, i.e., those compounds which, along with amines are always formed on amination of the corresponding alcohols with ammonia. The new experimental data introduced below provide a basis for more definite justification for the view that the catalytic synthesis of amines from alcohols and ammonia proceeds via spontaneous replacement of the hydroxyl group in an alcohol by an amino group with elimination of water:



EXPERIMENTAL

The experiments were carried out in a flow system apparatus which was described in a previous paper [2]. The vapors of the organic starting materials, plus ammonia at the required pressure, were passed through a chamber in a steel tube which contained the catalyst heated to the required temperature. The length of the catalyst layer in the tube was 35 cm, the weight of catalyst 45 g, and its apparent volume 75 ml. We chose to use as catalyst in all experiments a mixture of aluminum oxide (95%) and titanium oxide (5%) which has effective amination properties. The ammonia pressure, temperature, and flow rate were the same in all experiments and were respectively 8.5 atm, 370° and 0.37. The duration of the experiment was determined by the quantity of substances taken for the amination. It varied from one to three hours in the main.

All the liquid starting materials were prepared by two distillations. Their properties are given in the table.

The product of dehydration of butanol-1 on alumina at 380° was a mixture of butene-1 and butene-2. Analysis of this mixture for unsaturateds showed that it contained 98% olefines.

The catalyzate from the trap was stirred in a vessel with hydrochloric acid (diluted 1 : 3) and it was then worked up by the method described previously in our paper [1]. The quantity of saturated and unsaturated hydrocarbons and hydrogen was determined in the gaseous products in the gasometer. Carbon monoxide and dioxide were virtually absent from the gas mixture.

A chemical analysis was carried out on the catalyzate from the amination of butanol-1 and butyric acid in order to elucidate the composition of products formed by amination of the starting materials. A detailed analysis of the catalyzate obtained on aminating di-isoamyl ether was not carried out because of the low yield of amines.

Amination of butanol-1. 72 g of combined catalyzate (containing 1.40% amine nitrogen), obtained from the amination of butanol-1, was taken for analysis. From it 27.2 g of amine fraction and 34.0 g of non-amine fraction were separated. The amine fraction was fractionated at 754 mm many times to yield the following fractions:

Fraction I, b.p. 42-77°; 0.8 g; fraction II, b.p. 77-78°; 15.8 g; d_4^{20} 0.7408; n_D^{20} 1.3988; fraction III, b.p. 78-159°; 1.6 g; fraction IV, b.p. 159-161°; 3.4 g; d_4^{20} 0.7648; n_D^{20} 1.4087; fraction V, b.p. 161-215°; 2.2 g; fraction VI, b.p. 215-217°; 2.9 g; d_4^{20} 0.7782; n_D^{20} 1.4209; residue..... 2.5 g.

Properties of Substances Used in the Amination Experiments

Starting materials	B.p. °C (mm Hg)	d_4^{20}	n_D^{20}
Butanol-1	117-117.5 (757)	0.8092	1.3991
Butyraldehyde	75.5-75.8 (745)	0.8169	1.3835
Pentene-1	30-30.5 (756)	0.6409	1.3719
Octene-1	121-122 (749)	0.7150	1.4082
Di-isoamyl ether	172-172.5 (750)	0.7735	1.4078

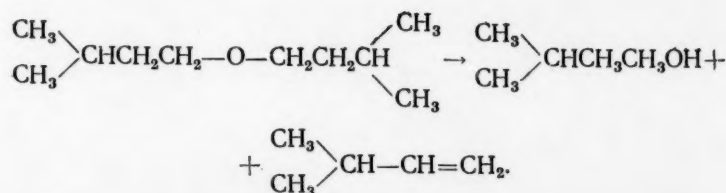
Elementary analysis of fractions II, IV, and VI showed the following carbon, hydrogen, and nitrogen contents: Fraction II. Calculated %: C 65.73; H 15.20; N 19.08. Calculated %: C 65.67; H 15.17; N 19.16. Fraction IV. Found %: C 74.45; H 14.63; N 10.67. Calculated %: C 74.33; H 14.83; N 10.84. Fraction VI. Found %: C 77.44; H 14.43; N 7.65. Calculated %: C 77.74; H 14.70; N 7.56.

According to their properties fractions II, IV, and VI are respectively n-butylamine [9], di-n-butylamine [10] and tri-n-butylamine [11].

Reductive amination of n-butyraldehyde. To carry out reductive amination of butyraldehyde approximately 1 mole of hydrogen per mole of aldehyde was introduced into the reaction tube together with the ammonia. From 102.1 g of catalyze (containing 1.62% amine nitrogen) obtained by the reductive amination of butyraldehyde under the conditions described above 12.3 g of amines was separated. The amine fraction was distilled at 751 mm. The following fractions were isolated: Fraction I, b.p. 36-77°, 0.8 g; fraction II, b.p. 77-79°, 6.2 g; d_4^{20} 0.7398; n_D^{20} 1.4002; fraction III, b.p. 78-156°, 1.1 g; fraction IV, b.p. 156-161°, 2.2 g; d_4^{20} 0.7655; n_D^{20} 1.4094; residue 1.0 g.

The elementary analysis of fractions II and IV gave in %: Fraction II. C 65.39; H 15.09; N 19.00. Fraction IV. C 74.22; H 14.36; N 10.23. The phenylthiourea derivatives obtained from the amine fractions II and IV melted at 64.5° and 70.6° respectively. On the basis of the data obtained it may be concluded that fraction II was mainly n-butylamine and fraction IV mainly di-n-butylamine.

Experiments on the direct amination of butyraldehyde in the absence of hydrogen did not give positive results. Only traces of amines were detected in the catalyze. None of the tests for the amino compounds, which normally accompany amines when the latter are synthesized from alcohols, was successful. Under the conditions in which up to 35-36% of amines (based on butanol taken) was obtained from butanol-1 and ammonia, a mixture of butenes, pentene-1, and octene-1 gave no amines. The yield of amines obtained by treating di-isoamyl ether with ammonia did not exceed 6%. This provides a basis for thinking that alkenes do not react with ammonia in the conditions chosen and hence they cannot be considered as intermediates in the amination of alcohols. The same applies to aldehydes and ethers. The formation of a small quantity of amines from di-isoamyl ether can be attributed to decomposition of the latter into alcohol and alkene.



In fact a small quantity of amylene was observed among the reaction products.

SUMMARY

1. The formation of amines from alcohols under the influence of ammonia takes place by simple substitution of amino groups for hydroxyl groups in the alcohol molecule with elimination of hydrogen.
2. Unsaturated hydrocarbons, aldehydes and simple ethers which are formed during the amination of alcohols are products of the side reactions, dehydration and dehydrogenation which occur on the surface of oxide catalysts at elevated temperatures.

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DEHYDRATION OF n-ALKANES ON THE CATALYST K-5

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The present investigation is a continuation of our study of dehydrogenation reactions of n-alkanes containing six or more carbon atoms [1, 2]. In these studies we succeeded in finding conditions for the selective dehydrogenation of n-hexane and n-nonane on a chrome-aluminum catalyst. However this reaction proceeds more selectively for n-decane on an industrial catalyst for n-butane dehydrogenation K-5, as we have shown previously [3].

It appeared interesting to study the behaviour of other alkanes in the presence of the catalyst K-5. To this end the n-alkanes from hexane to decane and also n-hexadecane were subjected to dehydrogenation on K-5 at 500° with a flow rate of 2.1 liters per hour. For comparison dehydrogenation experiments under the same conditions were carried out with cyclohexane and alkanes which are not able to undergo simple dehydrocyclization, e.g., n-pentane and isopentane. It was apparent that the catalyzates obtained from the n-alkanes C_6-C_{10} on the industrial catalyst K-5 contained several times as great a quantity of alkenes as of aromatic hydrocarbons. Most of the alkenes formed contained the same number of carbon atoms per molecule as the initial alkanes.

EXPERIMENTAL

All experiments were carried out with the same portion of catalyst (30 ml, 30.0 g, length of catalyst layer 16 cm in a quartz tube with an internal diameter of 20 mm) at 500°C with a hydrocarbon flow rate of 2.1 liters per hour. In each experiment the hydrocarbons were collected in 100 ml portions. The experiments lasted 95 min. With n-pentane, n-hexane, n-hexadecane and cyclohexane two experiments were run before regenerating the catalyst, with the other alkanes, three experiments. After distillation from sodium through a column of 40 theoretical plates all the initial hydrocarbons had constants which agreed with those in the literature. n-Hexadecane was separated from technical material by two distillations through a column under vacuum. It boiled within the limits 146-148° (8 mm); d_4^{20} 0.7742; n_D^{20} 1.4350. Literature data [4]; b.p. 188.7° (50 mm); d_4^{20} 0.7734, 0.7751; n_D^{20} 1.4345, 1.4352. The methods for carrying out the experiments and analyzing the catalyzates have been described in our previous papers [1, 2]. The results of some typical experiments from many similar ones are cited in the table.

On looking at the data in the table, the weak aromatizing ability of the catalyst is apparent. Only in the first experiment is any notable quantity of aromatic hydrocarbon obtained (up to 8%) and in the third experiment its production has practically ceased. Aromatic hydrocarbons were not obtained from n-hexane even in the first stage of the process. In the conditions chosen the yield of benzene from cyclohexane did not exceed 14%.

When n-pentane and isopentane were dehydrogenated (these hydrocarbons cannot undergo simple dehydrocyclization) the yield of alkenes was 9-10%. It should be noted that the activity of the catalyst K-5 in the dehydrogenation of isopentane is considerably less than the catalysts with which we carried out our earlier investigations. Thus, for example, from isopentane on an aluminum-chromium-potassium catalyst (catalyst-6) at 500° and a flow rate of 0.5 hr⁻¹ we obtained a catalyzate containing 40.3% alkenes, on an alumino-chrome catalyst (catalyst-4)-32.4%, but on catalyst K-5 only 26.6%. The composition and method of preparation of catalysts 4 and 6 is described in one of our papers [5]. However the aromatizing power of catalyst K-5 is considerably less than that of catalysts 4 and 6, and this is very important to us. Because of the relative yields of alkenes and aromatic hydrocarbons obtained from n-alkanes under the same conditions, it is better to carry out the dehydrogenation on catalyst K-5 than on catalysts 4 and 6.

As can be seen from the table 8-12% of alkenes is formed when n-alkanes with the composition C_6-C_{10} are dehydrogenated. In distinction from its aromatizing ability, the dehydrogenating activity of catalyst K-5 decreases more slowly from experiment to experiment. The alkene content of the catalyzate from experiment 3 is only 2-3%

Hydrocarbon	Experiment 1			Experiment 2			Experiment 3			Composition of gas from expt. 2, vol. %		
	Yield of catalyze n_D^{20}	content in catalyze, % al-kenes	gas in liters (NTP)	yield of catalyze	content in catalyze, % al-kenes	gas in liters (NTP)	yield of catalyze	content in catalyze, % al-kenes	gas in liters (NTP)	H ₂	C ₄ H ₁₀	C ₄ H ₁₀ +a
n-Pentane	97,0	9,4	2,400	97,6	8,0	2,270	96,0	7,7	1,750	97,3	—	2,7
2-Methylbutane	96,5	10,0	2,900	96,6	8,8	2,400	96,0	—	1,750	97,4	0,4	2,2
Cyclohexane	97,7	2,7	10,850	97,0	2,8	8,100	—	—	—	—	—	—
n-Hexane	97,7	8,3	3,500	97,9	8,5	3,350	—	—	—	98,2	0,2	4,6
n-Heptane	94,1	8,7	7,200	96,4	7,9	4,350	96,6	6,8	2,800	95,3	0,9	3,8
n-Octane	94,6	11,0	8,150	95,7	9,4	4,750	95,4	8,5	2,780	94,0	1,9	4,1
n-Nonane	95,4	11,9	6,400	97,0	10,5	3,660	97,6	8,6	2,300	84,1	9,5	6,4
n-Decane	96,4	12,8	6,300	97,8	10,5	4,050	97,3	9,7	2,000	89,2	3,5	7,3
n-Hexadecane	90,5	49,2*	7,600	89,4	45,4*	5,750	—	—	—	62,6	25,3	12,1

* Iodine number.

less than in the first experiment. n-Hexadecane underwent considerable cracking under our chosen reaction conditions. Therefore only the iodine number and the content of aromatic hydrocarbons in the catalyze are quoted in the table: the content of unsaturated hydrocarbons (which was determined on distillation fractions which were then summed) is discussed below.

The catalyzed from all the experiments for each hydrocarbon were combined and then fractionally distilled through a column of 40 theoretical plates. The chief aim was to determine the amount of cracking which accompanied dehydrogenation of the hydrocarbons. Some catalyzes and their fractions were analyzed by gas-liquid chromatography, coupled with combination dispersion spectroscopy.

The n-pentane catalyze with n_D^{20} 1.3600 distilled within the limits 30.0-37.0°. Gas-liquid chromatography showed that the catalyze contained 9.0-9.5% pentene-2, ~1% piperylene, ~2% isopentane, and unchanged n-pentane.

The isopentane catalyze with n_D^{20} 1.3560 contained 92% of isopentanes. The whole catalyze distilled within the limits 20.0-39.0°. By gas-liquid chromatography the catalyze was observed to contain, apart from unchanged isopentane, ~5% 2-methylbutene-2 and ~3% 2-methylbutene-1; a negligible quantity of 3-methylbutene-1 was possibly also present.

The cyclohexane catalyze, which boiled within the limits 72.5-82.0° and had n_D^{20} 1.4330, contained 2-4% cyclohexene and 12-13% benzene (determined by gas-liquid chromatography), besides unchanged starting material. Methylcyclopentane (1-2%) was observed distinctly by gas-liquid chromatography.

The n-hexane catalyze boiled within the limits 65.1-85.0° and had n_D^{20} 1.3785. By gas-liquid chromatography hexenes (8%—hexene-1 was absent) and less than 1% benzene were observed, apart from n-hexane. The presence of n-pentane, 2- and 3-methylpentanes, and cyclohexane were detected (less than 1% of each) in the catalyze by the same method.

The n-heptane catalyze with n_D^{20} 1.3930 boiled within the limits 90.3-111.0°. The catalyze and its separate fractions were analyzed by combination dispersion spectroscopy. Apart from n-heptane, 7-8% of heptenes (heptene-2 or heptene-3; heptene-1 was absent) and 2-3% toluene were observed.

The n-octane catalyze had n_D^{20} 1.4025 and contained 9.5% alkenes, calculated on C₈, and 3% aromatic hydrocarbons. On distillation of the catalyze a fraction was separated which boiled from 115.4 to 140.0° and which represented 97% of the total catalyze. Using combination dispersion spectroscopy octenes were observed (octene-1 was absent); according to the iodine number this fraction contained 8.2% alkenes, i.e., 86% of the total alkenes. The

low-boiling fraction 81.0-115.4° (1.6% by vol) contained 81% alkenes, calculated on C₇, i. e., 1.3% of the catalyzate. On the basis of the boiling limits of the fraction it can be considered that most of the alkenes in it are heptenes. Thus ~10% alkenes (of which 86% are octenes, and the remaining 14% more probably heptenes) are formed from n-octane under the conditions studied.

The n-nonane catalyzate with n_D^{20} 1.4110 contained 10.1% alkenes, calculated on C₉, and 3.0% aromatic hydrocarbons. Most of it (95.6%) boiled with the limits 145.0-156.0°. This fraction contained 87% of the total alkenes. Combination dispersion spectroscopy showed that it consisted of nonene-3 (less probably nonene-4) in cis- and trans-forms. Nonene-1 was absent from the catalyzate. The low boiling fraction 93.0-145.0° (3% by vol) contained 44% alkenes, i. e., 1.3% of the weight of the catalyzate or 13% of the total alkenes.

The n-decane catalyzate had n_D^{20} 1.4155; it contained 10.5% alkenes, calculated on C₁₀, and 3% aromatic hydrocarbons. On distillation a fraction was separated which boiled in the limits 100.0-163.5°, i. e., up to the boiling points of the decenes. This fraction was 2.5% by vol of the catalyzate and contained 73% alkenes; i. e., 2.0% of the catalyzate or 19% of the total alkenes. Most of the catalyzate (95%) boiled within the limits 163.5-180.5°. This fraction contained 9.0% alkenes, calculated on C₁₀. By combination dispersion spectroscopy it was established that decene-1 was absent from this fraction. Apparently the double bond in the decenes was at position 4 or 5. Thus a catalyzate containing 10% alkenes (81% decenes, and 19% lower alkenes) was formed from n-decane in the presence of the catalyst K-5 under the given conditions.

The n-hexadecane catalyzate. A sample of 150 ml of catalyzate with n_D^{20} 1.4365 was used for fractionation by distillation. It had an iodine number of 47.7 and contained 4.5% of aromatic hydrocarbons. A fraction (76% by vol) boiling in the limits 150-160° (10 mm) was separated. We considered this to be a hexadecane-hexadecene fraction because only constants for hexadecene-1 are to be found in the literature. This fraction contained 4.5% hexadecenes, i. e., 3.4% of the catalyzate by weight. Cracking products boiling up to 150° (12 mm) were separated (21.3%). This fraction contained 70% of unsaturated hydrocarbons—14.9% of the catalyzate by weight, they were distributed approximately as follows: C₅—1.0%; C₆—3.0%; C₇—1.9%; C₈—3.6%; C₉—C₁₅—5.4%. Thus the catalyzate from n-hexadecane contained 18.3% alkenes, 81.4% of which were cracking products and only 18.6% hexadecenes. In the C₅ and C₆ hydrocarbons the double bond was chiefly in position 1; this was demonstrated by gas-liquid chromatography. About 5% aromatic hydrocarbons were found in the n-hexadecane catalyzate. It is of interest to note that they were formed in the first 20-30 min of the experiment in a quantity of from 13 to 16% of the catalyzate; the content thereafter remained practically constant at ~3%.

Thus it is apparently possible to obtain 8-12% alkenes by dehydrogenation of n-alkanes (C₆—C₁₀) in the presence of the catalyst K-5. The larger part of the alkenes have the same number of carbon atoms in the molecule as the initial hydrocarbon. The alkenes formed from hexane and heptane consist almost solely of hexene and heptene respectively. The alkenes obtained from n-octane, n-nonane and n-decane were 87-81% octene, nonene and decene respectively, but 13-19% consisted of lower-boiling hydrocarbons. It should be noted that alkenes-1 were not found in the catalyzates of the alkanes studied. Only in the cracking products from n-hexadecane were alkenes found in which the double bond was in position 1.

The catalyst K-5 possesses weak aromatizing ability. By prolongation of the experiment (over 1.5 hr) without regenerating the catalyst one can avoid the formation of aromathydrocarbons almost completely. The isomerizing power of the catalyst is very low in the conditions studied. The paraffin part of the n-alkane catalyzates consists mostly of unchanged alkanes.

The detection of cyclohexane in the n-hexane catalyzate deserves mention. This was possible because gas-liquid chromatography was used. It was previously impossible to detect cyclanes at this level in the alkane conversion products from oxide catalysts.

SUMMARY

1. The dehydrogenation of n-alkanes of composition C₅—C₁₀, and also n-hexadecane and cyclohexane on the catalyst K-5 at 500° with a volume rate of 2.1 hr⁻¹ has been studied.
2. The n-alkane catalyzates obtained under these conditions contained 8-12% of the corresponding alkenes. n-Hexadecane underwent considerable cracking.
3. The catalyst possesses weak aromatizing and isomerizing power.

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THE ISOMERIZATION OF HIGHER n-PARAFFINES C₁₅ - C₁₈

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In the last three to five years, the attention of many investigators has turned to the isomerization of higher normal paraffine hydrocarbons into the corresponding low melting isoparaffines. The higher isoparaffines can be components of low setting fuels and also, based on them, there can be prepared special sorts of oils for friction in joints which work at low temperatures.

A basic obstacle for the isomerization of the higher paraffines is the side reaction of cracking. Thus, using the "traditional" isomerizing catalysts based on aluminum halides, prevention of the side reaction of cracking in the isomerization of the higher paraffines is possible only by the addition of large amounts of different cycloparaffine hydrocarbons [1]. Therefore all the existing work on isomerization of the higher paraffines is largely devoted to the selection of special catalysts on conditions to assure selective occurrence of the reaction. There is great interest in work on the isomerization of the higher paraffines carried out in the presence of bifunctional catalysts under pressure in hydrogen. Minachev and Shuikin with co-workers [2] have showed that in the presence of catalysts consisting of Pt, Pd, and Ni deposited on active aluminum oxide at a hydrogen pressure of 20-50 atm and a temperature of 350-460° the chief conversion of n-paraffines C₁₀-C₁₁ is the isomerization to the corresponding isoparaffines. The resulting isoparaffines were mono- and dimethyl substituted alkanes. From a study of the catalysts they showed that platinized aluminum oxide activated by hydrofluoric acid showed great selectivity. Petrov and co-workers [3] studied the isomerization of alkanes with the composition of C₁₂-C₁₃ in the presence of a catalyst of 0.5% Pt-Al₂O₃ activated by HF; here also it was shown that the reaction occurs with formation of mono and dimethyl substituted isomers, with predominance of the latter which agreed well with the calculated data obtained by the authors. It is important to note that the isomerization was still accompanied by considerable cracking: the yield of products with molecular weight equal to that of the starting paraffines C₁₅-C₁₆ was on the order of 50-60%. In the work of other investigators [4] it was shown that in isomerization of solid paraffines in the presence of a Pt-Al₂O₃ catalyst activated by hydrochloric acid, the cracking reaction was considerably decreased by the use of a high molar ratio of hydrogen to raw material and higher hydrogen pressures. Unfortunately, investigations in the field of isomerization of higher paraffines have been limited to these studies and to a series of patent reports [5].

In the present work we give the results of a study of the reaction of isomerization of paraffines with composition C₁₅-C₁₈ in the presence of an industrial catalyst based on tungsten sulfide. It is known that these catalysts have chiefly been studied in the reactions of splitting and hydrogenation of hydrocarbons of different classes, and there is only a single example of their use for isomerization of low molecular weight paraffine hydrocarbons [6].

EXPERIMENTAL

In this work we used industrial sulfide catalysts WS₂, WS₂-NiS-Al₂O₃, and WS₂ + aluminosilicate*. For the isomerization we took a mixture of paraffines with composition C₁₅-C₁₈, and also in one of the studies of the catalysts we carried out the isomerization of n-octadecane. The properties of the starting products are given in Table 1.

The fraction of n-paraffines C₁₅-C₁₈ was isolated by vacuum distillation from technical cetane. In Fig. 1 we give the distillation curve of the mixture of n-paraffines C₁₅-C₁₈ used. n-Octadecane was obtained by hydrogenation of pure normal octadecyl alcohol (b.p. 59°) in the presence of the catalyst WS₂-NiS-Al₂O₃ at 280-290° and an initial hydrogen pressure of 150 atm.

*These catalysts are known in industry under the names: WS₂, contact 5058; WS₂-NiS-Al₂O₃, contact 8376; and WS₂-aluminosilicate, contact 5058.

TABLE 1. Properties of the Starting Products Used in Isomerization

Hydrocarbon	B.p., °C mm Hg	n_D^{20}	d_4^{20}	Molec. wt.	Setting temp. °C
n-Paraffines, C ₁₅ -C ₁₈	272-324 (760)	1,4377	0,7792	236	+18
n-Octadecane	158-159 (7)	1,4350*	0,7763	256	+27,7, 28,5

* Found at 30°.

TABLE 2. Isomerization of n-Paraffines of Composition C₁₅-C₁₈ in the Presence of Sulfide Catalysts under a Pressure of 20 atm

Expt. No.	Catalyst	Temp- erature °C	Volume rate, hrs ⁻¹	Molar ratio, H ₂ /paraf- fine	Yield of liquid pro- ducts, wt. %	Composition of catalyzate, %		
						cracking products (fraction to 240°)	unconver- ted n- paraffines	isoparaf- fines
1	WS ₂	380	1,45	7,5	85,8	44,0	26,4	29,5
2	The same	390	1,54	8,6	80,0	39,7	30,7	29,5
3	»	380	1,45	15,8	91,0	30,0	35,4	35,6
4	»	390	1,64	22,0	88,0	11,0	65,3	23,2
5	WS ₂ +NiS+Al ₂ O ₃	384	1,50	9,0	94,0	12,4	56,8	30,8
6	The same	385	1,49	12,6	96,0	9,1	73,4	17,5
7	»	400	1,55	12,4	97,0	8,2	65,1	26,7
8	»	432	1,60	12,4	91,5	16,3	58,3	30,4
9	»	450	1,56	11,9	95,0	23,2	41,9	34,9
10	WS ₂ +alumino- silicate	383	1,50	8,4	84,5	42,7	48,6	8,7

TABLE 3. Properties of Resulting Isoparaffines C₁₅-C₁₈

Expt. No.	Boiling range, °C at 760 mm Hg	n_D^{20}	d_4^{20}	Molec. wt.	Temp. of beginning crystalliza- tion, °C	Setting temp., °C
1	250-315	1,4434	0,7894	218	-43	-64
2	242-315	1,4522	0,7995	210	-41	-65
3	240-320	1,4426	0,7841	220	-42	-64
4	242-315	1,4450	0,7898	220	-31	-48
5	238-306	1,4388	0,7862	232	-51	-72
6	250-316	1,4393	0,7885	232	-47	-60
7	238-212	1,4388	0,7865	233	-45	-60
8	240-312	1,4408	0,7918	226	-47	-67
9	238-310	1,4425	0,7928	228	-45	-66
10	242-310	1,4410	0,7712	223	-36	-64

Isomerization of n-paraffines was studied in a circulating apparatus under a hydrogen pressure of 20 atm. n-Paraffines and hydrogen, first heated to 160-180°, were fed at a definite rate into the reactor which contained 250 ml of ground catalyst (diameter of particles 1-3 mm). The reaction product passed from the reactor through a condenser into a high pressure receiver, and the gas was discharged into the atmosphere. In all the experiments, for partial suppression of the cracking reaction, we added 3% benzene to the starting paraffines. The inhibiting action of benzene in amounts not above 3% on the cracking reaction was established in preliminary autoclave experiments on isomerization of n-paraffines C₁₂-C₁₆ in the presence of WS₂.

Since we were first of all interested in isomers with molecular weight equal to that of the starting compounds, we did not study the cracking products. We considered the cracking products to be the fraction of catalyzate boiling up to 240°, that is, to the temperature at which possible isoparaffines with composition $C_{15}-C_{18}$ would boil. The isoparaffines with composition $C_{15}-C_{18}$ were obtained by a two fold carbamide purification of the catalyzate fraction boiling above 240°; here by decomposition of the complexes the starting n-paraffines $C_{15}-C_{18}$ were again evolved.

In Tables 2 and 3 we give the main results on isomerization of a mixture of n-paraffines $C_{15}-C_{18}$ in the presence of different sulfide catalysts.

On the WS_2 catalyst we first found the optimum value for the reaction temperature of 380-400° and the rate of supplying the raw product of 1.5 hr⁻¹. With these conditions and a mole ratio of hydrogen to paraffine of 7.5 (experiment 1) the resulting catalyzate contained about 30% isoparaffines $C_{15}-C_{18}$, 26% of unconverted n-paraffines, and 44% of cracking products. Using higher mole ratios of hydrogen to paraffine led to a considerable fall in yield of cracking products. This is immediately apparent from the data of Fig. 2. With increase in molar ratio of hydrogen to paraffine to 22, the content of cracking products in the catalyzate fell to 11%. Increase in the molar ratio is not always favorable for the isomerization reaction. Thus, if increase in ratio of hydrogen to paraffine from 7.5 to 15.8 (experiments 1-3) occurs along with fall in content of cracking products and increased yield of isoparaffines, yet at

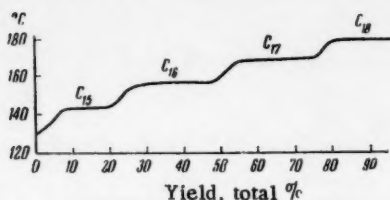


Fig. 1. Curve of vacuum distillation of the starting paraffines $C_{15}-C_{18}$ (19 mm 25 theoretical plates).

a ratio of hydrogen to paraffines equal to 22 there is a simultaneous drop in both content of cracking products and yield of isoparaffines in the catalyzate. An analogous effect occurs with increased mole ratio of hydrogen to paraffine for the setting temperature of the resulting isoparaffines (Table 3). Thus, at mole ratios of hydrogen to paraffine in the range 7.5-15.8 isoparaffines are obtained which set in about the same range (-41 to -65°), but at higher ratios of hydrogen to paraffine (to 22 in experiment 4) there is a marked rise in setting temperature of the isoparaffines (-31 to -48° in experiment 4). Thus, varying the range of mole ratios of hydrogen to paraffine can considerably hinder the side cracking reactions, but at very high ratios there is a simultaneous hindering of both the cracking reaction and the isomerization.

Isomerization on a $WS_2-NiS-Al_2O_3$ catalyst is accompanied by considerably less cracking. Thus, under the same conditions (experiments 5 and 2) in the presence of $WS_2-NiS-Al_2O_3$ the content of cracking products in the catalyzate was almost 3.5 times less than in the catalyzate obtained in the presence of WS_2 . Although in both cases practically the same yield of isoparaffines was reached (on the order of 30%), the $WS_2-NiS-Al_2O_3$ catalyst permitted the formation of more low-setting isomer (Table 3). It is interesting that increased mole ratio of hydrogen to paraffine from 9 to 12.6 in the presence of $WS_2-NiS-Al_2O_3$ led to almost twice the lowering in yield of isoparaffines (experiments 5 and 6); however, the effect of increased mole ratio of hydrogen to paraffine in this case was greatly weakened with rise in reaction temperature (Fig. 3). Due to the weak cracking ability of the $WS_2-NiS-Al_2O_3$ catalyst we could carry out the isomerization reaction over a rather wide range of temperature. Thus, even at 450° the content of cracking products in the catalyzate reached only 23% with a yield of isoparaffines of 35%.

We should note that in its selectivity for the reaction of isomerization of the paraffines of the composition mentioned, the $WS_2-NiS-Al_2O_3$ catalyst greatly surpassed bifunctional catalysts based on Pt and Pd. The other catalyst, WS_2 -aluminosilicate under these conditions caused chiefly the reaction of splitting the starting paraffines and also possibly formation of isoparaffines with composition $C_{15}-C_{18}$. From the catalyzate obtained with this catalyst we isolated only 8.4% isoparaffines $C_{15}-C_{18}$ with a content of cracking products of about 43%.

Isomerization of n-octadecane was carried out in the presence of the $WS_2-NiS-Al_2O_3$ catalyst at 420° with a volume rate 1.5 hr⁻¹, mole ratio $H_2/n-C_{18}H_{38}$ equal to 11, and pressure of 20 atm. In this case we added 3% benzene. Preliminary distillation of the catalyzate showed that from the molecular weight, the cracking products corresponded to the fraction boiling to 280°. The fraction of the catalyzate with composition C_{18} (above 280°) was studied by the methods described. In Table 4 we give the results of isomerization of n-octadecane under the conditions used.

As Table 4 shows, isomerization of n-octadecane also occurs with formation of a rather low setting isomer. The slight increase in content of cracking products compared to the preceding experiments on the same catalyst could

TABLE 6. Results of Spectral Study of Narrow Fractions of the Isoparaffines Obtained in the Presence of $WS_2-NiS-Al_2O_3$

Boiling range, °C at 20 mm Hg	Molec wt.	Infrared spectra data		
		No. of CH_2 groups	No. of CH_3 groups	Type of isomer
118 —138	200	9	4	DMS
138 —142	210	9	4	"
142 —145	210	9	3,5	DMS + MMS
145 —150	218	10	4	DMS
150 —152	223	10	4	"
152 —154	220	10	4	"
154 —157	224	10	4	"
157 —160	227	10	3,5	DMS ^a + MMS
160 —164,5	232	10,5	4	"
164,5 —165,5	236	11	4	"
165,5 —169	238	11,5	3,5	MMS + DMS
169 —173	245	11,5	4	DMS
173 —175	248	12	4	"
175 —184	250	12	3,5	DMS + MMS

^aDMS, dimethyl substituted isomer; MMS, monomethyl substituted isomer.

TABLE 7. Results of a Spectral Study of Isomers of Octadecane Obtained in the Presence of $WS_2-NiS-Al_2O_3$

Boiling range, °C at 20 mm Hg	Molec wt.	Infrared spectra data			Boiling range °C at 20 mm Hg.	Molec wt.	Infrared spectra data		
		# of CH_2 groups	# of CH_3 groups	type of iso- mers			# of CH_2 groups	# of CH_3 groups	type of isomers
155—169	245	—	—	—	177 —179	252	12	4	DMS
169—173	246	12	4	DMS	179 —180,5	247	12	4	"
173—175	246	12	4	"	180,5—181	249	13	3,5	DMS
175—177	247	12	4	"	181 —183	247	14	3	+ MMS MMS

The average branching of the narrow fractions of isoparaffines obtained in the presence of WS_2 was determined by the ratio of optical density of the bands in the region of 3.35-3.51 according to the method of [7]. As Table 5 shows, isomerization in the presence of WS_2 goes with formation of a mixture of mono- and dimethyl substituted isomers, and under conditions of hindering the isomerization reaction under the influence of a high mole ratio of hydrogen to paraffine there is formation chiefly of the monomethyl substituted isomer.

The average branching of isoparaffines obtained in the presence of $WS_2-NiS-Al_2O_3$ was determined by a somewhat modified method [8], according to which we carried out a calculation of the intensity of absorption in the region corresponding to CH_2-CH_3 oscillation by which we calculated the total number of CH_2 and CH_3 groups, and in the final calculation, determined the type of isomer.

As Table 6 shows, isomerization of n-paraffines $C_{15}-C_{18}$ in the presence of the $WS_2-NiS-Al_2O_3$ catalyst also occurs with formation of di- and monomethyl substituted isomers, with predominance of isomers of the first type.

The isomers of octadecane were studied by an analogous method. As the results in Table 7 show, isomerization of n-octadecane in the presence of $WS_2-NiS-Al_2O_3$ also occurred with preferential formation of the dimethyl substituted isomers.

SUMMARY

1. We have studied the isomerization of higher n-paraffines $C_{15}-C_{18}$ on sulfide catalysts.

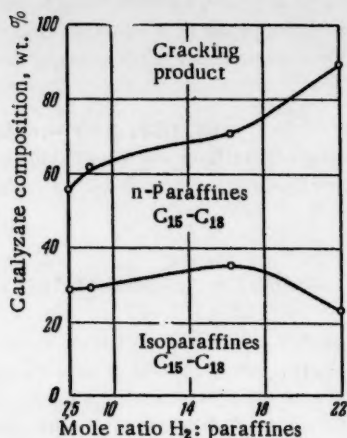


Fig. 2. Effect of mole ratio of hydrogen to paraffine on composition of isomerization products in the presence of WS_2 .

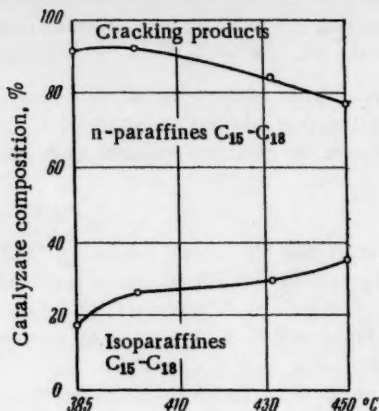


Fig. 3. Effect of temperature of the reaction on composition of isomerization products in the presence of $WS_2-NiS-Al_2O_3$.

TABLE 4. Results of Isomerization of n-Octadecane in the Presence of $WS_2 - NiS - Al_2O_3$ (420° , 1.5 hr^{-1} , $H_2/n-C_{18} = 11, 20 \text{ atm.}$)

Yield of catalyzate, wt. %	Composition of catalyzate, wt. %			Properties of isooctadecane					
	cracking products (fraction to 280°)	$n-C_{18}H_{38}$	isooctadecane	boiling range $^\circ C$ (7 mm)	n_D^{20}	d_4^{20}	molec. wt.	temp. of beginning crystallization, $^\circ C$	setting temp., $^\circ C$
91	40	36.3	23.7	134 - 163	1.4452	0.8022	247	-42	-52

TABLE 5. Results of Spectrum Study of the Narrow Fractions of Isoparaffines Obtained in the Presence of WS_2

Boiling range °C at 7 mm Hg	Molec. wt.	Infrared spectral data		Boiling range °C at 7 mm Hg	Molec. wt.	Infrared spectral data	
		No. of CH ₂ groups	No. of CH ₃ groups in side chain			No. of CH ₂ groups	No. of CH ₃ groups in side chain
Isoparaffines, exper. 1				Isoparaffines, exper. 4			
117-126	212	9	2	131-135	207	12	1
129-134	216	11	1	138-143	222	12	1
139-144	224	9,5	2	143-147	238	12	1,5
144-147	226	11,5	1	147-150	235	12,5	1
147-150	238	14	1	150-155	227	13	1

first of all be explained by the fact that in the isomerization of n-octadecane cracking would occur much more intensely than in the case of the paraffines $C_{15}-C_{18}$. Judging by the setting temperature, the resulting isoparaffine corresponds chiefly to mono- and dimethyl substituted isomers. In view of the large number of possible isomers of this type, it was impossible to make a detailed study of their composition and so we were limited to determination of the degree of branching of the isoparaffines from the infrared absorption spectra. The isoparaffines for this purpose were distilled into narrow fractions of a column with the effectiveness of 25 theoretical plates. The results of the spectral study are given in Tables 5-7.

2. At 380-400° and under a hydrogen pressure of 20 atm. on an $WS_2-NiS-Al_2O_3$ catalyst there is transformation of n-paraffines $C_{15}-C_{18}$ into the isoparaffines of the same composition with yields of 26-35%. Under optimum conditions cracking products compose not more than 8-12%; 56-66% of the n-paraffines are not changed and can be used again in the reaction.

3. Isomerization of the n-paraffines, as was shown by investigation of the spectra, takes place with formation of mono- and dimethyl substitution; the freezing temperature of the starting n-paraffines was 18-27°, and the freezing temperature of the paraffines obtained after isomerization was -42 to -52°.

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THE REACTION OF ISOTOPIC EXCHANGE OF HYDROGEN WITH ALKYL HALIDES

II. HYDROGEN EXCHANGE WITH TERTIARY ALKYL CHLORIDES

IN ANHYDROUS ACETIC ACID IN THE PRESENCE OF LEWIS ACIDS

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In previous communications [1, 4] we have observed that tert-butyl chloride reacts by hydrogen exchange with acetic acid in the presence of Lewis acids FeCl_3 , SbCl_5 , SnCl_4 , ZnCl_2 , HgCl_2 . In the absence of the Lewis acids, hydrogen exchange with acetic acid does not occur. A study of the kinetics of this reaction permitted us to establish the activity of the different Lewis acids in the reaction of hydrogen exchange. It was shown that the greatest activating action in the reaction of hydrogen exchange of tert-butyl chloride was by ferric chloride and antimony chloride and the least by mercuric chloride. Investigation of the Lewis acids by their effect on the rate of hydrogen exchange of tert-butyl chloride in deuterioacetic acid arranged them in the following order: $\text{FeCl}_3 \geq \text{SbCl}_5 > \text{SnCl}_4 > \text{ZnCl}_2 > \text{HgCl}_2$.

TABLE 1

Hydrogen Exchange of Alkyl Chlorides (Molecular Ratio of Components R-Cl :
: CH_3COOD : $\text{MeCl}_n = 1: 10: 0.1$)

Lewis acid	$K \cdot 10^7 \cdot \text{sec}^{-1}$				Lewis acid	$K \cdot 10^7 \cdot \text{sec}^{-1}$			
	20°	25°	30°	40°		20°	25°	30°	40°
2-Chloro-2-methylpentane					1-Chloro-1-methylcyclohexane				
FeCl_3	630	1160	1970	—	FeCl_3	1320	1930	3040	—
SbCl_5	510	1000	1950	—	SbCl_5	530	1140	2210	—
SnCl_4	130	210	500	—	SnCl_4	204	350	620	1780
ZnCl_2	—	61	107	430	ZnCl_2	—	110	250	650
HgCl_2	—	4,4	10	40	HgCl_2	—	8	16	39
BF_3	1	—	3	14	Without a catalyst	No ex-change	0,4	0,7	1,4
Without a catalyst	0,16	—	0,63	—					

It is important to explain whether their order is maintained in the reaction of hydrogen exchange of tertiary alkylchlorides with different structures. For this purpose we studied the kinetics of hydrogen exchange of 2-chloro-2-methylpentane and 1-chloro-1-methylcyclohexane in anhydrous acetic acid in the presence of the Lewis acids FeCl_3 , SbCl_5 , SnCl_4 , ZnCl_2 , HgCl_2 , and BF_3 . The rate constants of hydrogen exchange were determined at several temperatures in the presence of varying amounts of Lewis acids. The results of the study are given in Table 1. Under the same conditions we found the rate constants of hydrogen exchange of tertiary alkyl chlorides with different structures as shown in Tables 2-4.

The investigation showed that the rate constants of hydrogen exchange in the tert-alkyl chlorides studied actually depend on the structure of the alkyl group, since we found an increase in rate of exchange of hydrogen with the alkyl chlorides with increase in their molecular weight. It is interesting to note that Ingold and co-workers found a similar tendency in comparing the rates of solvation of tert-alkyl chlorides which occurred by the S_N^1 mechanism [2].

TABLE 2. Hydrogen Exchange of Different Alkyl Chlorides in Deuteroacetic Acid in the Presence of SnCl_4 (ratio of components $\text{RCl}:\text{CH}_3\text{COOD}:\text{SnCl}_4 = 1:10:0.1$)

Temperature °C	$K \cdot 10^7 \cdot \text{sec}^{-1}$			Ratio of constants $K_3:K_2:K_1$
	tert-butyl chloride K_1	2-chloro- 2-methyl- pentane, K_2	1-chloro-1- methyl- cyclohexane, K_3	
20	40	130	204	5:3:1
25	59	210	351	6:4:1
30	123	500	620	5:4:1
40	382	—	1780	5:—:1

TABLE 3. Hydrogen Exchange of Alkyl Chlorides in Deuteroacetic Acid in the Presence of SbCl_5 (molar ratio of components $\text{RCl}:\text{CH}_3\text{COOD}:\text{SbCl}_5 = 1:10:0.1$)

Temperature °C	$K \cdot 10^7 \cdot \text{sec}^{-1}$			Ratio of constants $K_3:K_2:K_1$
	tert-butyl chloride, K_1	2-chloro- 2-methyl- pentane, K_2	1-chloro- 1-methyl- cyclohexane, K_3	
20	151	510	530	3,5:3,4:1
25	311	1000	1140	3,5:3,2:1
30	717	1250	2240	3,1:2,7:1

TABLE 4. Hydrogen Exchange of Alkyl Chlorides in Deuteroacetic Acid in the Presence of FeCl_3 (mole ratio of components $\text{RCl}:\text{CH}_3\text{COOD}:\text{FeCl}_3 = 1:10:0.05$)

Temperature, °C	$K \cdot 10^7 \cdot \text{sec}^{-1}$		K_2/K_1	Temperature, °C	$K \cdot 10^7 \cdot \text{sec}^{-1}$		K_2/K_1
	tert-butyl chloride, K_1	1-chloro- 1-methyl- cyclohexane, K_2			tert-butyl chloride, K_1	1-chloro- 1-methyl- cyclohexane, K_2	
20	102	390	3.8	30	294	971	3.3
25	177	585	3.3	40	618	2270	3.7

TABLE 5. Relative Activities of Lewis Acids in the Reaction of Hydrogen Exchange of tert-Alkyl Chlorides* (mole ratio $\text{RCl}:\text{CH}_3\text{COOD}:\text{MeCl}_n = 1:10:0.1$)

Temp °C	BF_3	HgCl_2	ZnCl_2	SnCl_4	SbCl_5	FeCl_3
2-Chloro-2-methylpentane						
20	$\frac{1}{3}$	—	—	50	200	240
25	—	1	14	48	230	260
30	$\frac{1}{3}$	1	11	50	200	200
40	$\frac{1}{3}$	1	11	—	—	—
		1	12	49	240	230
1-Chloro-1-methylcyclohexane						
25	—	1	14	44	144	240
30	—	1	16	39	138	190
40	—	1	17	46	—	—
		1	16	43	140	220

*The value for the rate constant of hydrogen exchange of alkyl chlorides in the presence of HgCl_2 was conditionally taken as unity.

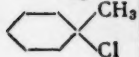
The relative activity of Lewis acids studied in the reaction of hydrogen exchange in 2-chloro-2-methylpentane and 1-chloro-1-methylcyclohexane is shown in Table 5.

As the results in Table 5 show, the most active among the Lewis acids are ferric chloride and antimony chloride. There is unexpectedly low activity in acetic acid in the reaction of hydrogen exchange with boron fluoride. This is probably explained by the fact that BF_3 forms a very stable molecular compound with acetic acid, $2\text{CH}_3\text{COOH} \cdot \text{BF}_3$, in which the boron atom is coordinately saturated and hence under these conditions BF_3 is not a Lewis acid.

It is of interest to compare the relative activities of the Lewis acids from the data of kinetics of hydrogen exchange of the different tert-alkyl chlorides which we studied: tert-butyl chloride, 2-chloro-2-methylpentane, and 1-chloro-1-methylcyclohexane (Table 6).

The data shown in Table 6 indicate that the relative activity of the different Lewis acids is maintained practically constant for both aliphatic chlorides and differs only slightly for the alicyclic chloride. It is established that in acetic acid the activity of ferric chloride and antimony pentachloride is 20 times higher than the activity of zinc chloride, and tin chloride is four times more active than

TABLE 6. Relative Activities of Lewis Acids in Acetic Acid

Alkyl chloride	Lewis acid			
	ZnCl ₂ *	SnCl ₄	SbCl ₅	FeCl ₃
(CH ₃) ₃ CCl	1	4	21	23
(CH ₃) ₂ C-Cl	1	4	18	19
	1	3	9	14

* The rate constant of hydrogen exchange of alkyl chlorides in the presence of ZnCl₂ was conditionally taken as unity.

ZnCl₂ was described in communication I [1]. BF₃, obtained by the method of Meerwein and Panwitz [3] was absorbed by acetic acid and in this form fed into the reaction.

Experiments on hydrogen exchange of tertiary alkyl chlorides. The experiments on hydrogen exchange of 2-chloro-2-methylpentane and 1-chloro-1-methylcyclohexane were carried out in the same way as the experiments with tert-butyl chloride described in [1]. The alkyl chlorides were separated from a sample taken by pouring it into ice water. Since all the kinetic experiments were carried out under similar conditions, we limit the description to only a few of them.

2-Chloro-2-methylpentane in acetic acid in the presence of FeCl₃. We dissolved 0.71 g (4.37 mMole) of FeCl₃ in 26.15 g (435 mMole) of deuterioacetic acid (11230 γ/ml) which contained 0.6% acetic anhydride. The solution was placed in a thermostat at 25° and 5.30 g (43.6 mMole) of 2-chloro-2-methylpentane was added. Samples were poured into ice water, washed with a 1-3% potash solution, and dried over CaCl₂.

Time of taking sample, min	Relative density γ/ml	$K \cdot 10^4 \cdot \text{sec}^{-1}$	$K_{av} \cdot \text{sec}^{-1}$
25	685	1,30	
30	725	1,16	
35	765	1,07	1,16 · 10 ⁻⁴
40	885	1,10	

2-Chloro-2-methylpentane in acetic acid in the presence of BF₃. In a solution which contained 0.19 g BF₃ (2.81 mM) and 16.75 g (279 mM) of deuterioacetic acid we placed 3.32 g (27.4 mM) of 2-chloro-2-methylpentane. The samples were collected and treated in the same way as in the previous experiment.

Time of taking sample, hours	Relative density γ/ml	$K \cdot 10^6 \cdot \text{sec}^{-1}$	$K_{av} \cdot \text{sec}^{-1}$
10	183	1,40	
20	377	1,52	
30	522	1,41	1,48 · 10 ⁻⁶
48	900	1,61	

1-Chloro-1-methylcyclohexane in acetic acid in the presence of FeCl₃. We placed 0.88 g (5.5 mM) of FeCl₃, 31.98 g (5.34 mM) of deuterioacetic acid (9960 γ/ml) and 6.94 g (52.4 mM) of 1-chloro-1-methylcyclohexane in a thermostat at 20.2°. Samples of 1-chloro-1-methylcyclohexane were taken in the usual way.

* Carried out with participation of laboratory assistants A. N. Astakhova, L. E. Andreeva, and A. I. Golovanova.

zinc chloride under the same conditions. We assume that by using the method of hydrogen exchange we can reach a quantitative estimation of the activities of different Lewis acids which play such an important part in organic chemistry.

EXPERIMENTAL*

Deuteroacetic acid was prepared by hydrolysis of acetic anhydride with deuterium oxide and contained 0.4-0.6% acetic anhydride.

Alkyl chlorides: 2-chloro-2-methylpentane, b.p. 42° (64 mm), n_D^{20} 1.4133; d_4^{20} 0.8625, and 1-chloro-1-methylcyclohexane, b.p. 58° (30 mm), n_D^{20} 1.4572; d_4^{20} 0.9669, were prepared from the corresponding carbinols by treatment with hydrochloric acid.

Lewis acids we used commercial C. P. chlorides of the metals FeCl₃, SbCl₅, SnCl₄, ZnCl₂, HgCl₂. C. P. FeCl₃ and HgCl₂ were not further purified. Purification of SnCl₄, SbCl₅, and

Time of taking sample, sec	Relative density γ/ml	$K \cdot 10^4 \text{ sec}^{-1}$	$K_{av} \cdot \text{sec}^{-1}$
960	422	1,48	
1800	808	1,63	$1,32 \cdot 10^{-4}$
2700	900	1,23	
3540	1130	1,24	

1-Chloro-1-methylcyclohexane in acetic acid in the presence of SnCl_4 . We placed 1.03 g (3.95 mM) of SnCl_4 , 23.82 g (397 mM) of deuterioacetic acid (9960 γ/ml), and 5.18 g (391 mM) of 1-chloro-1-methylcyclohexane in a thermostat at 20.2°. The samples of alkyl chloride were collected in the usual way.

Time of taking sample, min	Relative density γ/ml	$K \cdot 10^{-5} \cdot \text{sec}^{-1}$	$K_{av} \cdot \text{sec}^{-1}$
187	665	2,11	
240	790	2,01	$2,04 \cdot 10^{-5}$
306	948	1,99	

SUMMARY

1. We have studied the kinetics of hydrogen exchange in 2-chloro-2-methylpentane and 1-chloro-1-methylcyclohexane in anhydrous acetic acid in the presence of the Lewis acids: FeCl_3 , SbCl_5 , SnCl_4 , ZnCl_2 , HgCl_2 , and BF_3 . Under the same conditions, the rate constants of hydrogen exchange in the alkyl chlorides depend essentially on their structures.

2. On the basis of the results of hydrogen exchange in different tert-alkyl chlorides we have arranged a series of relative activities $\text{FeCl}_3 \approx \text{SbCl}_5 > \text{SnCl}_4 > \text{ZnCl}_2 > \text{HgCl}_2 > \text{BF}_3$.

3. The relative activities of the different Lewis acids remain constant for the tert-aliphatic chlorides and differ only somewhat for the alicyclic chloride.

4. We have suggested that the method of hydrogen exchange is suitable for quantitative estimation of the Lewis acids.

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THE REACTION OF ISOTOPIC EXCHANGE OF HYDROGEN WITH ALKYL HALIDES

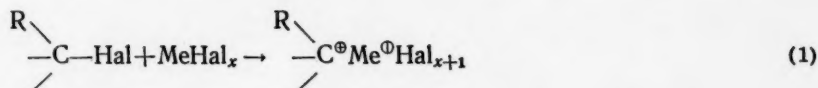
III. THE ROLE OF LEWIS ACIDS IN REACTIONS OF HYDROGEN EXCHANGE BY TERTIARY ALKYL CHLORIDES

V. N. Setkina and D. N. Kursanov

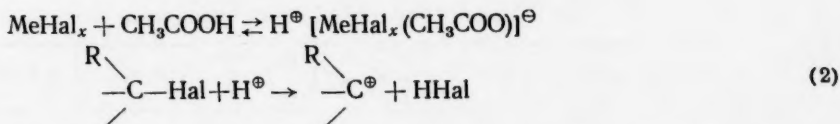
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As already reported, [1], we have found that addition of Lewis acids, halides of coordinately unsaturated metals, to acetic acid solutions of tert-alkyl chlorides causes their hydrogen exchange, while in the absence of Lewis acids hydrogen exchange does not occur. The explanation of the activating action of Lewis acids in the reaction of hydrogen exchange of alkyl chlorides is based on the idea that the Lewis acids act by heterolysis of the carbon-chlorine bond and hydrogen exchange in these cases depends on formation of a carbonium ion. However, heterolysis of the C-Hal bond in alkyl halides under the influence of Lewis acids in an acetic acid medium can be explained in two ways:

1. The ability of the Lewis acid in reaction with alkyl halide to complete its valence shell by coordination with the halide anion (scheme I)



2. The formation of strong complex acids by reaction of the Lewis acid with acetic acid. In this case, heterolysis of the C-Hal bond should be capable of raising the proton concentration, that is, the activating action of the Lewis acid in this case will depend on increasing the concentration of hydrogen ions (scheme 2)



The significance of these two factors in the heterolysis of the C-Hal bond by the influence of the Lewis acid can be estimated by comparing the rate of hydrogen exchange of alkyl halides in two media with the same acidity, but differing by the presence of a Lewis acid in one of them. For an answer to this question we carried out a kinetic study of the reaction of hydrogen exchange of tert-butyl chloride and 1-chloro-1-methylcyclohexane in anhydrous acetic acid, enriched by deuterium, in the presence of different amounts of ZnCl_2 or SnCl_4 . Data on the acidity of solutions of ZnCl_2 and SnCl_4 in acetic acid has recently been published by Satchell [4]. At the same time we studied the kinetics of hydrogen exchange of tert-butyl chloride in deuterioacetic acid which contained different amounts of sulfuric acid or hydrogen chloride. The acidity of solutions of H_2SO_4 in anhydrous acetic acid was studied in 1940 by Hall and Spengeman [5] and of hydrogen chloride in acetic acid, by Satchell in 1958 [4].

From the results on acidity of solutions of ZnCl_2 , SnCl_4 , H_2SO_4 , and HCl in acetic acid we can compare the rates of hydrogen exchange of tert-alkyl halides in these solutions at very similar values of acidity. The results of study of the kinetics of hydrogen exchange of tert-alkyl chlorides under different conditions are given in Tables 1-4. In Tables 5 and 6 we compare the results on hydrogen exchange of tert-alkyl chlorides in different systems ($\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$, $\text{CH}_3\text{COOH} + \text{ZnCl}_2$, $\text{CH}_3\text{COOH} + \text{HCl}$, $\text{CH}_3\text{COOH} + \text{SnCl}_4$), which have similar values for acidity.

TABLE 1. Hydrogen Exchange of tert-Butyl Chloride in Anhydrous Acetic Acid in the Presence of ZnCl_2 at 25° (mole ratio chloride: acetic acid = 1:10)

ZnCl_2 conc. (in mole ratio chloride:acetic acid = 1:10)	Acidity of solution, $\lg I^*$	$K \cdot 10^7 \cdot$ $\cdot \text{sec}^{-1}$	ZnCl_2 conc. (in mole per 1000 g CH_3COOH)	Acidity of solution, $\lg I^*$	$K \cdot 10^7 \cdot \text{sec}^{-1}$
0,171	—	20	0,667	—0,47	133
0,256	—1,28	26	0,827	—0,32	222
0,336	—1,16	84	1,161	—0,07	382
0,336	—1,16	86	1,563	+0,23	557
0,598	—0,57	128	1,404	+0,11	484**

* I is ionization of 4-chloro-2-nitroaniline in $\text{CH}_3\text{COOH}-\text{ZnCl}_2$ [4].

** Interpolated value.

TABLE 2. Hydrogen Exchange of tert-Butyl Chloride in Anhydrous Acetic Acid in the Presence of H_2SO_4 (mole ratio chloride: acetic acid = 1:10)

H_2SO_4 conc. (in mole per 1000 g CH_3COOH)	Tempera- ture, °C	Acidity function H_0^*	$\lg I$	$K \cdot 10^7 \cdot$ $\cdot \text{sec}^{-1}$
0,169	30,1	—1,74	—0,984**	1,0
0,327	30,1	—2,30	—	1,1
0,778	30,1	—2,88	—	1,5
0,344	25	—2,32	+1,48***	0,8
0,665	25	—2,80	—	1,4
0,916	25	—2,98	—	1,6
1,460	25	—3,20	—	4,8

* Values of H_0 taken from paper [7].

** For 4,4-dimethoxydiphenylmethanol [8]

*** For 4-chloro-2-nitroaniline [6]

TABLE 3. Hydrogen Exchange of tert-Alkyl Chlorides in Anhydrous Acetic Acid in the Presence of HCl (mole ratio chloride: acetic acid = 1:10)

Alkyl chloride	HCl conc. (in mole per 1000 g CH_3COOH)	Temp. °C	$\lg I^*$	$K \cdot 10^7 \cdot \text{sec}^{-1}$
tert-butyl chloride	0,283	25	+0,58	Обмена прак- тически нет
“	0,82	25	+1,48	“
“	0,82	30	+1,48	0,4
1-chloro-1-methyl- cyclohexane	0,817	30,2	+1,47	1,3

* For 4-chloro-2-nitroaniline [4].

Our investigation showed that at the same initial acidities of the medium in systems which contained Lewis acids ($\text{CH}_3\text{COOH} + \text{ZnCl}_2$, $\text{CH}_3\text{COOH} + \text{SnCl}_4$) and those which did not contain Lewis acids ($\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$, $\text{CH}_3\text{COOH} + \text{HCl}$) the rate of hydrogen exchange of tert-alkyl chlorides was markedly different. Actually, hydrogen exchange occurred very much faster under those conditions where Lewis acids were present.

TABLE 4. Hydrogen Exchange of tert-Alkyl Chlorides in Anhydrous Acetic Acid in the Presence of SnCl_4 (mole ratio chloride: CH_3COOH = 1: 10)

Alkyl chloride	SnCl_4 conc. (in mole per 1000 g CH_3COOH)	Temp. °C	lg I*	$K \cdot 10^7 \cdot \text{sec}^{-1}$
Tert-butyl chloride	0,167	25	+1,48	62
	0,167	30	+1,48	120
1-Chloro-1-methylcyclohexane	0,167	25	+1,48	350
"	0,167	30	+1,48	620

*For 4-chloro-2-nitroaniline.

TABLE 5. Hydrogen Exchange of tert-Butyl Chloride in Media which Have Similar Acidity Values

Components of media	Temp., °C	lg I	$K \cdot 10^7 \cdot \text{sec}^{-1}$
I $\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$	25	-0,984*	0,8
$\text{CH}_3\text{COOH} + \text{HCl}$	25	-0,98*	No exchange
$\text{CH}_3\text{COOH} + \text{ZnCl}_2$	25	-0,94*	
II $\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$	30	+1,48**	1,1
$\text{CH}_3\text{COOH} + \text{HCl}$	30	+1,48	0,4
$\text{CH}_3\text{COOH} + \text{SnCl}_4$	30	+1,48	120

*For 4,4-dimethoxydiphenylmethanol [8].

**For 4-chloro-2-nitroaniline [6].

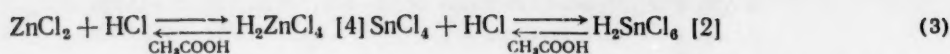
TABLE 6. Hydrogen Exchange of 1-Chloro-1-methylcyclohexane in Media which Have Similar Initial Activities

Component of the medium	Temp., °C	lg I	$K \cdot 10^7 \cdot \text{sec}^{-1}$
$\text{CH}_3\text{COOH} + \text{H}_2\text{SO}_4$	30	+1,48*	1,9
$\text{CH}_3\text{COOH} + \text{HCl}$	30	+1,48	1,3
$\text{CH}_3\text{COOH} + \text{SnCl}_4$	30	+1,48	620

*For 4-chloro-2-nitroaniline [4].






On the basis of the data which we obtained we can conclude that the activity of the Lewis acids in the reaction of hydrogen exchange of tert-alkyl chlorides in acetic acid depended not so much on change in acidity of the medium, due to formation of complex acids, as on the ability of the Lewis acids to complete their valence shells with the chlorine atom of the tert-alkyl chloride in accordance with scheme (1). These ideas agree well with the experimental results on weak activity of BF_3 in CH_3COOH [2] since under these conditions, BF_3 forms a stable proton acid $\text{BF}_3 \cdot 2\text{CH}_3\text{COOH}$ in which the boron atom is coordinatively saturated.

To confirm these ideas, we were interested in studying how decreased coordination unsaturation of the same Lewis acid could be reflected in the results of hydrogen exchange of the alkyl chlorides. We took advantage of the results of Satchell and co-workers [4, 6] who showed that the acidity function in solutions of tin chloride and zinc chloride in acetic acid increased in the presence of hydrogen chloride due to formation of a strong complex acid H_2ZnCl_2 and H_2SnCl_2 (scheme 3)



Thus the decrease in coordination unsaturation of the Lewis acids under these conditions was accompanied by a rise in the acidity function of the solutions. We compared the kinetics of hydrogen exchange of tert-alkyl chlorides (tert-butyl chloride and 1-chloro-1-methylcyclohexane) in acetic acid in the presence of Lewis acids (SnCl_4 , SbCl_5 , FeCl_3) with the kinetics of hydrogen exchange of the same chlorides in analogous conditions, but with the presence of hydrogen chloride. It was shown that the rate constant of hydrogen exchange of the alkyl chlorides decreased 1.5-2 times in the presence of hydrogen chloride (Table 7). Hence, the decrease in coordination unsaturation of Lewis acids lessened their activity in the reaction of hydrogen exchange of alkyl chlorides even under those conditions in which the acidity of the medium was increased. This agrees well with our ideas on the mechanism of activating action of Lewis acids in the reaction of hydrogen exchange of alkyl chlorides.

TABLE 7. Effect of Hydrogen Chloride on the Reaction of Hydrogen Exchange of tert-Alkyl Chlorides in Acetic Acid in the Presence of Lewis Acids

Alkyl chloride	MeHal _x	Molar ratio RCl: CH ₃ COOH:MeHal _x : HCl	Temp., °C	K · 10 ⁷ · sec ⁻¹
(CH ₃) ₃ C-Cl	FeCl ₃	1 : 10 : 0,05 : 0,09	30	199
(CH ₃) ₃ C-Cl	FeCl ₃	1 : 9 : 0,05 : 0	30	303
	SnCl ₄	1 : 10 : 0,12 : 0,3	30	570
	SnCl ₄	1 : 10 : 0,12 : 0	30	900
	SbCl ₅	1 : 10 : 0,05 : 0,03	25	380
	SbCl ₅	1 : 10 : 0,05 : 0,05	25	340
	SbCl ₅	1 : 10 : 0,05 : 0	25	570

Comparison of the results obtained in the study of the reaction of hydrogen exchange of alkyl halides with different structures in acid media with high ionizing ability [9] and also in media with small ionizing ability, but in the presence of Lewis acids [1] gave us a basis for considering that hydrogen exchange of the alkyl halides was due to the heterolysis of the bond C-Hal and formation of the carbonium ion. At the present time, however, we have not arranged the necessary experimental materials so as to estimate at what stage of ionization of the alkyl halide the hydrogen exchange occurs; whether it occurs in the stage of formation of the ionic complex, the ion pair, or solvation of the carbonium ion.

EXPERIMENTAL

The experiments on hydrogen exchange of tert-alkyl chlorides were carried out in media of deuterioacetic acid which contained 1-2% acetic anhydride. Addition of Lewis acids and taking of the samples were carried out in an atmosphere of dry nitrogen. A detailed description of the experiments is given in communication I [2], and II [3]. tert-Butyl chloride was isolated from the collected samples by vacuum distillation (at the temperature of the given experiment). 1-Chloro-1-methylcyclohexane was isolated from the reaction mixture by pouring the sample into ice water. The values of the rate constant of hydrogen exchange of alkyl chlorides were calculated from 4-6 determinations.

SUMMARY

1. The activity of Lewis acids in the reaction of hydrogen exchange of tert-alkyl chlorides in acetic acid depends on the ability of the Lewis acids to complete their valence shells with atoms of chlorine from tert-alkyl chlorides, which leads to ionization of the carbon-halogen bond.

2. Change in acidity of the medium due to formation of complex acids in the reaction of Lewis acids with acetic acid had subordinate value in the reaction of hydrogen exchange under these conditions.

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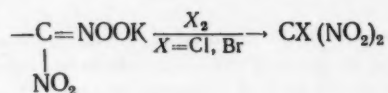
THE PREPARATION AND QUANTITATIVE DETERMINATION OF α -HALOGEN SUBSTITUTED NITROCOMPOUNDS

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One of the best methods for identifying nitro compounds is their conversion to the corresponding halogen derivatives. In the present work this method is used for the identification of 1,1-dinitroalkanes and 1,1,3,3-tetranitroalkanes which we have synthesized. These alkanes were converted into the potassium salts which were then chlorinated or brominated.



The halogen derivatives which we obtained were analyzed for halogen content by the iodometric method. This method is based on the oxidizing power of the halides bound to the dinitromethyl group; in the reaction of such halides with potassium iodide, free iodine is liberated and this is then titrated with thiosulfate. In 1903 Meisenheimer [1] used this method for analysis of 2-bromo-2,2-dinitro-1-ethoxyethane. Later Klager [2] suggested the use of iodometry as a general method for analysis of compounds which contained the bromodinitromethyl group.

In attempting to use the method of Klager for quantitative determination of the compounds described in the present work we found that by this method we could not get satisfactory results for some of our substance. This fact led us to a systematic study of the iodometric determination of halonitro derivatives which contained the bromo- and chlorodinitromethyl group.

For the systematic study we obtained in addition to the chloro and bromo derivatives of 1,1-dinitroalkanes and 1,1,3,3-tetranitroalkanes which have been mentioned, also 1,2-dichloro-1,1,2,2-tetranitroethane and 1,1,2-tribromo-1,2,2-trinitroethane. The starting substances for preparing these two compounds were the dipotassium salts of symmetrical tetranitroethane [3, 4].

The constants of the compounds which contain chloro and bromo dinitromethyl groups and which were studied in this work are given in Table 1.

These compounds were analyzed for halogen content by the iodometric method. Titration was carried out in aqueous alcohol in the presence of starch as the indicator.

Klager [2] recommends use of 50% methanol as the medium. However, we find that in such a medium, due to the comparatively high alcohol concentration, the color of the starch is weak and very unstable, as has also been reported in the handbooks of iodometry. The best medium for titration seems to be 30% ethanol. In this solvent, the monobromo derivatives, 1-bromo-1,1-dinitroalkanes and 1-bromo-1,1,3,3-tetranitroalkanes, react quantitatively with potassium iodide; the iodine which is evolved is sharply titrated with thiosulfate. 1,1,2-tribromo-1,2,2-trinitroethane behaves in an analogous manner. As would be expected, two of the three bromine atoms in this compound enter the reaction.

In the reaction of 1,3-dibromo-1,1,3,3-tetranitropropane with potassium iodide in 30% ethanol reaction does not go to conclusion so that the results of the analysis for bromine are low. Unsatisfactory results are also found in the titration in the presence of sulfuric acid, as often occurs in iodometric titrations. In this case during the titration

TABLE 1. Constants of the α -Halonitrocompounds

Name	Formula	Yield %	B.p., °C. (press. mm Hg)	M.p., °C	n_D^{20}	d_4^{20}	MR		Literature data
							found	calc.	
1-Chloro-1,1-dinitroethane	$\text{CH}_3\text{CCl}(\text{NO}_2)_2$	64, 8	48, 5 (12)	—	1, 4438	1, 4729	27, 86	27, 54	B.p. 59—61° (22 mm), n_D^{20} 1, 4439, d_4^{20} 1, 465 [6]
1-Bromo-1,1-dinitroethane	$\text{CH}_3\text{CBr}(\text{NO}_2)_2$	74, 7	65, 5 (15)	—	1, 4764	1, 8481	30, 39	30, 41	B.p. 49—50° (4, 7 mm), n_D^{20} 1, 4757, d_4^{20} 1, 831 [6]
1-Chloro-1,1,1-dinitropropane	$\text{C}_2\text{H}_5\text{CCl}(\text{NO}_2)_2$	100	47—48, 5 (8)	—	1, 4445	1, 3737	32, 62	32, 16	—
1-Bromo-1,1,1-dinitropropane	$\text{C}_2\text{H}_5\text{CBr}(\text{NO}_2)_2$	90, 2	74, 5 (12)	—	1, 4736	1, 7077	35, 04	35, 06	—
1-Chloro-1,1,1-dinitrobutane	$\text{C}_3\text{H}_7\text{CCl}(\text{NO}_2)_2$	65, 9	62, 5 (7)	—	1, 4467	1, 3165	37, 04	36, 81	—
1-Bromo-1,1,1-dinitrobutane	$\text{C}_3\text{H}_7\text{CBr}(\text{NO}_2)_2$	90, 3	76, 5—77(7)	—	1, 4714	1, 6042	39, 58	39, 71	—
1-Bromo-1,1-dinitro-2-methylpropane	$(\text{CH}_3)_2\text{CHCBr}(\text{NO}_2)_2$	53, 1	—	25	—	—	—	—	M.p. 38° [7]
1-Chloro-1,1,1-dinitropentane	$\text{C}_4\text{H}_9\text{CCl}(\text{NO}_2)_2$	74, 3	84, 5—85 (10)	—	1, 4485	1, 2620	41, 74	41, 46	—
1-Bromo-1,1,1-dinitropentane	$\text{C}_4\text{H}_9\text{CBr}(\text{NO}_2)_2$	80, 7	81, 5 (4)	—	1, 4712	1, 5233	44, 27	44, 35	—
4-Bromo-4,4-dinitro-2-methylbutane	$(\text{CH}_3)_2\text{CHCH}_2\text{CBr}(\text{NO}_2)_2$	46, 8	95 (12)	—	1, 4712	1, 5220	44, 30	44, 38	—
1-Chloro-1,1-dinitrohexane	$\text{C}_5\text{H}_{11}\text{CCl}(\text{NO}_2)_2$	58, 4	95, 5 (10)	—	1, 4500	1, 2196	46, 40	46, 10	—
1-Bromo-1,1-dinitrohexane	$\text{C}_5\text{H}_{11}\text{CBr}(\text{NO}_2)_2$	59, 7	100, 5 (7)	—	1, 4706	1, 4557	48, 96	48, 99	—
1-Chloro-1,1,1,3,3-tetranitrobutane	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{CCl}(\text{NO}_2)_2$	100	—	32	—	—	—	—	[8]
1-Bromo-1,1,1,3,3-tetranitrobutane	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{CBr}(\text{NO}_2)_2$	100	—	47	—	—	—	—	[8]
1-Chloro-1,1,3,3-tetranitropentane	$\text{C}_3\text{H}_5\text{C}(\text{NO}_2)_2\text{CH}_2\text{CCl}(\text{NO}_2)_2$	100	—	8—10	1, 4905	1, 5650	52, 99	53, 04	—
1-Bromo-1,1,3,3-tetranitropentane	$\text{C}_3\text{H}_5\text{C}(\text{NO}_2)_2\text{CH}_2\text{CBr}(\text{NO}_2)_2$	93	—	13—14	1, 5056	1, 7753	55, 37	55, 74	[8]
1,3-Dichloro-1,1,3,3-tetranitropropane	$(\text{NO}_2)_2\text{CClCH}_2\text{CCl}(\text{NO}_2)_2$	100	—	36—37	—	—	—	—	—
1,3-Dibromo-1,1,3,3-tetranitropropane	$(\text{NO}_2)_2\text{CBrCH}_2\text{CBr}(\text{NO}_2)_2$	100	—	69—70	—	—	—	—	[8]
1,2-Dichloro-1,1,2,2-tetranitroethane	$(\text{NO}_2)_2\text{CClCCl}(\text{NO}_2)_2$	85, 7	—	95—96	—	—	—	—	M.p. 107° [3]
1,1,2-Tribromo-1,1,2-trinitroethane	$\text{NO}_2\text{CBr}_2\text{CBr}(\text{NO}_2)_2$	38, 9	—	119—120	—	—	—	—	M.p. 124—125° [4]
Chlorotrinitromethane	$(\text{NO}_2)_3\text{CCl}$	85	56 (40)	—	1, 4500	1, 6769	29, 73	28, 57	M.p. 51, 5—52° (30 mm) d_4^{20} 1, 681 [9]
Bromotrinitromethane	$(\text{NO}_2)_3\text{CBr}$	90	74 (32)	—	1, 4808	2, 0313	32, 21	31, 47	B.p. 55—56° (12 mm), d_4^{20} 2, 0443 [9]
Iodotrinitromethane	$(\text{NO}_2)_3\text{CI}$	50	—	53—54	—	—	—	—	d_4^{20} 2, 0443 [9]
Bromodinitroacetic ester	$(\text{NO}_2)_2\text{CBrCOOC}_2\text{H}_5$	31	69—70 (3)	—	1, 4635	1, 6934	41, 84	41, 26	M.p. 58° [10] 56° [11]

there is a continuous restoration of color of iodine which makes impossible the determination of the equivalent point. However, in the reaction of 1,3-dibromo-1,1,3,3-tetranitropropane with potassium iodide in the presence of acetic or boric acids the reaction goes quantitatively and iodine is evolved sharply for titration with thiosulfate; restoration in color does not occur.

We also studied iodometric titration of compounds which contained the chlorodinitromethyl group. It should be noted that iodometric determination of such compounds is not described in the literature. We showed that 1-chloro-1,1-dinitroalkanes practically did not react with potassium iodide even in the presence of sulfuric acid. On the other hand, 1-chloro-1,1,3,3-tetranitroalkanes quantitatively oxidized potassium iodide, like the corresponding bromides. 1,2-Dichloro-1,1,2,2-tetranitroethane also reacted easily with potassium iodide, but the quantitative reaction occurred only on addition of acid with a dissociation constant on the order of 10^{-5} (for example, 1,1-dinitroethane). Reaction occurred spontaneously with potassium iodide in the case of 1,3-dichloro-1,1,3,3-tetranitropropane; only one of the two chlorine atoms reacted, independent of whether the determination was carried out without acid or in the presence of weak acids (acetic, boric). The data on the quantitative determination of halogens in chloro- and bromodinitro-methyl derivatives is given in Table 2.

TABLE 2. Quantitative Determination of Halogen by the Iodometric Method in α -Halodinitro Compounds

Name	Formula	Halogen content, %	
		found	calculated
1-Bromo-1,1-dinitroethane	$C_2H_3N_2O_4Br$	39,74; 39,73	40,16
1-Bromo-1,1-dinitropropane	$C_3H_5N_2O_4Br$	36,99; 37,12	37,02
1-Bromo-1,1-dinitrobutane	$C_4H_7N_2O_4Br$	35,03; 34,98	35,21
1-Bromo-1,1-dinitro-2-methylpropane	$C_4H_7N_2O_4Br$	35,25	35,21
1-Bromo-1,1-dinitropentane	$C_5H_9N_2O_4Br$	32,92; 32,89	33,16
4-Bromo-4,4-dinitro-2-methylbutane	$C_6H_{11}N_2O_4Br$	32,97	33,16
1-Bromo-1,1-dinitrohexane	$C_6H_{11}N_2O_4Br$	31,08; 31,16	31,33
1-Chloro-1,1,3,3-tetranitrobutane	$C_4H_5N_4O_8Cl$	12,81; 12,74	13,01
1-Bromo-1,1,3,3-tetranitrobutane	$C_4H_5N_4O_8Br$	25,46; 25,49	25,22
1-Chloro-1,1,3,3-tetranitropentane	$C_5H_7N_4O_8Cl$	12,29; 12,26	12,37
1-Bromo-1,1,3,3-tetranitropentane	$C_5H_7N_4O_8Br$	23,89; 23,99	24,14
1,3-Dichloro-1,1,3,3-tetranitropropane	$C_3H_3N_4O_8Cl_2$	12,09; 12,23	24,21
1,3-Dibromo-1,1,3,3-tetranitropropane	$C_3H_3N_4O_8Br_2$	41,44; 41,50	41,84
1,2-Dichloro-1,1,2,2-tetranitroethane	$C_2H_2N_4O_8Cl_2$	25,45; 25,22	25,42
1,1,2-Tribromo-1,2,2-trinitroethane	$C_2H_2N_3O_8Br_3$	39,81; 39,76	59,66
Chlorotrinitromethane	CN_3O_6Cl	18,79; 18,74	19,12
Bromotrinitromethane	CN_3O_6Br	34,64; 34,37	34,75
Iodotrinitromethane	CN_3O_6J	45,51; 45,57	45,83
Bromodinitroacetic ester	$C_4H_5N_2O_8Br$	31,28; 31,25	31,11

These results can serve as a criterion of the oxidizing ability of the halide with respect to potassium iodide in the study of halodinitromethyl derivatives. As would be expected, bromides are more reactive than chlorides. We showed in this respect that 1-chloro-1,1-dinitroalkanes did not react at all with potassium iodide while 1-bromo-1,1-dinitroalkanes oxidized potassium iodide quantitatively. The presence of the nitro group in position 2 or position 3 with respect to the halodinitromethyl group permitted reactivity of the halide, as was evident from comparison of inactive 1-chloro-1,1-dinitroalkanes with 1-chloro-1,1,3,3-tetranitroalkanes which reacted quantitatively with potassium iodide. The effect of the nitro group in position 2 was shown more strongly than in position 3. Thus, in 1,2-dichloro-1,1,2,2-tetranitroethane both atoms of chlorine reacted quantitatively, with potassium iodide, and in 1,3-dichloro-1,1,3,3-tetranitropropane, only one atom.

We also studied iodometric analysis of the halotrinitromethanes. Attempts to titrate these compounds with potassium iodide under the usual conditions, in aqueous alcohol, did not succeed, since the determination of the equivalent point was impossible because of the very rapid return of the iodine color*. We found that chloro-, bromo-, and iodotrinitromethane could be analyzed quantitatively if titration was carried out in a medium buffered at pH 7. Titration in a buffer solution can evidently be used in iodometric determination of other halodinitro

*There is evidence in the literature of the possibility of iodometric titration of bromonitroform [5] in an ordinary, unbuffered medium, which our experiments did not confirm.

derivatives which are characterized, like the halonitroforms, by an especially strong oxidizing activity toward potassium iodide. Thus, bromodinitroacetic ester, also studied in our work, was titrated quantitatively under these conditions. The data on the quantitative determination of the halonitroforms and bromodinitroacetic ester are given in Table 2 and the constants of these compounds in Table 1.

Thus, on the basis of the results of our work we can conclude that in the iodometric determination of α -halodinitro compounds the conditions of titrations should depend on the nature of the compound. The first group of compounds, titrated quantitatively is 30% alcohol, consists of 1-bromo-1,1-dinitroalkanes and 1-chloro-1,1,3,3-tetranitroalkanes. The second group consists of compounds with more active halogens, chloro-, bromo-, and iodotrinitromethanes and also bromodinitroacetic ester; these compounds should be titrated in a buffer at pH 7. Finally, in the third group we find dihalogenides, which must be titrated in weakly acid solutions.

As the data of Table 1 show, chloro- and bromotrinitromethane have an exalted molecular refraction which is characteristic for compounds of such a type [12]. Bromodinitroacetic ester resembles the halotrinitromethanes in this respect.

EXPERIMENTAL

Preparing chloro- and bromo derivatives. Chloro and bromo derivatives were obtained by chlorination or bromination of the corresponding potassium salts under a layer of ether with energetic stirring and cooling with ice. The ether solution was dried with calcium chloride, evaporated in a vacuum, and the residue consisted of the halogen derivative. 1-Chloro- and 1-bromo-1,1-dinitroalkanes, bromodinitroacetic ester, and also chloro- and bromotrinitromethanes were purified by distillation. 1-Chloro-1,1,3,3-tetranitrobutane was recrystallized from hexane at 25-27°, 1-bromo-1,1,3,3-tetranitrobutane, from carbon tetrachloride or hexane at 40°, 1-chloro- and 1-bromo-1,1,3,3-tetranitropentane were dissolved in hexane at room temperature with later freezing out 1,3-dichloro-1,1,3,3-tetranitropropane was recrystallized from hexane at 30°, 1,3-dibromo-1,1,3,3-tetranitropropane from tetrachloroethane at 35° (in the presence of activated charcoal), 1,2-dichloro-1,1,2,2-tetranitroethane from octane at 40°, 1,1,2-tribromo-1,2,2-trinitroethane from boiling chloroform, iodotrinitromethane from octane with later freezing out. The constants of the resulting compounds are given in Table 1.

TABLE 3

Name	Formula	Halogen content, %	
		found	calculated
1-Chloro-1,1-dinitropropane	$C_3H_5N_2O_4Cl$	20,49; 20,79	21,04
1-Chloro-1,1-dinitrobutane	$C_4H_7N_2O_4Cl$	19,22; 19,40	19,42
1-Chloro-1,1-dinitropentane	$C_5H_9N_2O_4Cl$	18,50; 18,35	18,04
1-Chloro-1,1-dinitrohexane	$C_6H_{11}N_2O_4Cl$	16,68; 16,78	16,84
1,2-Dichloro-1,1,2,2-tetranitroethane	$C_2H_2N_4O_8Cl_2$	25,73; 25,89	25,42
1,3-Dichloro-1,1,3,3-tetranitropropane	$C_3H_2N_4O_8Cl_2$	24,53; 24,62	24,21

Iodometric titrations. We dissolved 0.15-0.2 g of halogen derivatives in 20 ml of ethanol, added 2 g of potassium iodide, and after 1-2 minutes added 40 ml of distilled water and titrated with 0.1 N thiosulfate solution in the presence of starch. In the determination of halotrinitromethanes and bromodinitroacetic ester along with the distilled water we took 40 ml of citrate-phosphate buffer (pH 7). In the case of 1,3-dibromo-1,1,3,3-tetranitropropane before titration we added boric acid (about 1 g) or glacial acetic acid (5-6 drops); in the case of 1,2-dichloro-1,1,2,2-tetranitroethane we added gem-dinitroethane (5-6 drops).

The results of the iodometric determinations of the halogen derivatives are given in Table 2. Also some of the chloro derivatives were analyzed by the combustion method. These results are given in Table 3.

SUMMARY

1. We have obtained a number of new compounds which contain the chloro- or bromodinitromethyl group.
2. We have studied the iodometric determination of these halogen derivatives and also of the halotrinitromethanes. The conditions for the quantitative determination of α -halodinitro compounds should be set up depending on the nature of the compounds.

3. With the help of the iodometric method we can analyze quantitatively compounds which contain one or two bromodinitromethyl groups, and also chloro derivatives which have not less than two dinitromethyl groups. Chloro-, bromo-, and iodotrinitromethanes can also be analyzed quantitatively by the iodometric method.

4. On the basis of the results obtained we have drawn conclusions on the relative oxidizing power of the halogens in the compounds studied, with respect to potassium iodide.

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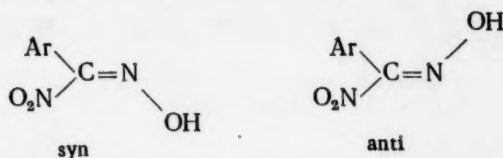
REACTIONS OF N_2O_4 WITH ORGANIC COMPOUNDS

VII. SYN AND ANTI-ISOMERS OF ARYLNITROLIC ACIDS

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Original article submitted January 14, 1960

In one of the previous communications [1] we showed that arylnitrolic acids could exist in two forms which differed from each other in physical and some chemical properties, and we suggested that the existence of the two forms of arylnitrolic acids could be explained by syn-anti-isomerism



In the present work we have also used spectroscopic methods to convince ourselves that our substances actually have the structure of nitrolic acids. For this purpose we have taken the infrared absorption spectra of both forms of p-nitro- and p-chlorobenznitrolic acids and the first form of m-nitro- and o-nitrobenznitrolic acids in dichloroethane solution (Table 1). Photography was carried out in the regions $1300\text{--}1700\text{ cm}^{-1}$ and $2800\text{--}3500\text{ cm}^{-1}$ on an IKS-11 spectrometer with prisms of NaCl and LiF.

TABLE 1. Valence Oscillation Frequencies of the Nitro Group, Hydroxyls, and $\text{C}=\text{N}$ Bonds of Arylnitrolic Acids in Dichloroethane Solutions

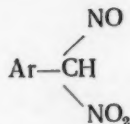
Substance		Valence oscillation* of nitrogroups (cm ⁻¹)				Valence oscil- lation of hydroxyl, cm ⁻¹	Valence oscil- lation of C=N bond, cm ⁻¹
		in side chain		in ring			
		symmetri- cal	antisym- metrical	symmetri- cal	anti- sym- me- trical		
p-Chlorobenznitrolic acid	Form I	—	1553 s			3510 m	1635 w
	Form II	1352 m	1551 s			3510 m	1635 w
p-Nitrobenznitrolic acid	Form I	—	1555 s	1342 m	1530 s	3510 m	••
	Form II	—	1552 s	1341 m	1533 s	3510 m	••
m-Nitrobenznitrolic acid	Form I	—	1550 s	1342 sh	1540 s	3500 m	1620 m
o-Nitrobenznitrolic acid	Form I	—	1557 s	1338 m	1540 s	3510 m	1623 m
Ethylnitrolic acid***		1344 s	1562 s			3281 s	1640 w
Propylnitrolic acid		1345 s	1545 s			3355 s	1665 w

*s, strong; w, weak; m, medium; sh, shoulder.

**Lines not produced, due to low solubility of substance

***Literature data (in Nujol) [2].

Table 1 shows that in the spectra there are all three chief structural elements of nitrolic acids*: nitro groups in the side chain, hydroxyls, and C=N bonds. This fact, along with the absence of characteristic valence oscillation frequencies of the C-H bond and tertiary carbon atom excludes the other possible isomeric structure, that of an aryl nitronitrosomethane.



In a previous communication [4] we described preparing compounds to which we ascribed the structure of aryl-nitronitrosomethanes; they differed in properties from both forms of nitrolic acids. The spectrum of one of them,

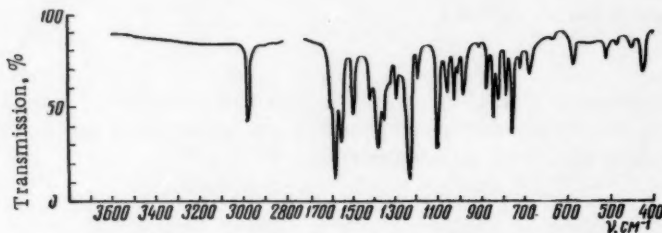
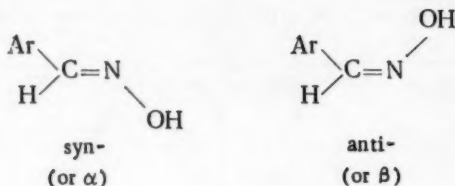


Fig. 1. Infrared absorption spectrum of p-chlorophenylnitronitrosomethane in the regions 400-1700 and 2800-3600 cm^{-1} .

p-chlorophenylnitronitrosomethane, confirmed the assumed structure; the spectrum had the oscillation frequencies of the CH group (2980 cm^{-1}) and the nitro group in the side chain (symmetrical 1376 cm^{-1} and antisymmetrical 1551 cm^{-1}) and lacked the oscillation frequencies of hydroxyl and C=N bonds (Table 2 and Fig. 1).

To test the assumption of syn-anti-isomerism of the nitrolic acids as the cause of the existence in two forms we made a comparison of the infrared absorption spectra of both forms of p-chlorobenznitrolic acid with the spectra of syn and anti-p-chlorobenzaldoximes



The oximes were chosen for comparison because they were very similar in structure to the nitrolic acids. The literature also described in great detail the differences between the infrared absorption spectra of the syn- and anti-isomers of the aromatic aldioximes [5, 6]. It is natural to assume that analogous differences should occur also in the spectra of the two forms of nitrolic acids, if these forms are actually syn and anti-isomers.

Since differences in the spectra are found only in the solid forms of the oximes (suspended in Nujol), and not in their solutions, in taking the spectra of the nitrolic acids, these were used in solid form; we used the same method for comparison in taking the oxime spectra. Samples were prepared in the form of disks by pressing a mixture of the substance and KBr. Photography of the spectra of these disks was carried out in a UR-10 infrared spectrometer in the region 400-1700 and 2800-3400 cm^{-1} . The spectra are shown in Figs. 2-5, frequencies in Tables 2 and 3. For comparison we took from the resulting spectra only the most reliable frequencies: the oscillation frequency of the

* This confirms that the water contained in the m-nitrobenznitrolic acid [3] does not enter chemically into the composition of the organic molecule, but is water of crystallization.

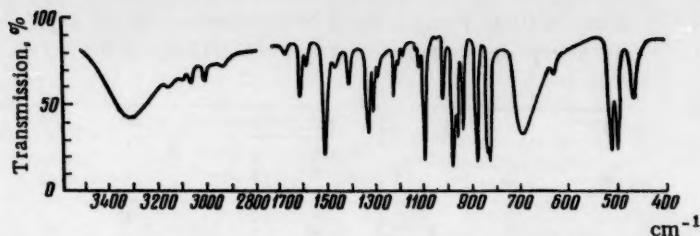


Fig. 2. Infrared absorption spectrum of syn-p-chlorobenzaldoxime in the region 400-1700 and 2800-3600 cm^{-1} .

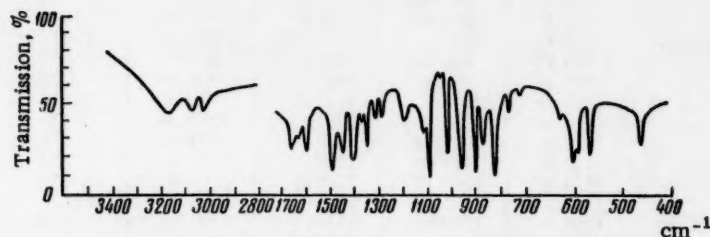


Fig. 3. Infrared absorption spectrum of anti-p-chlorobenzaldoxime in the region 400-1700 and 2800-3600 cm^{-1} .

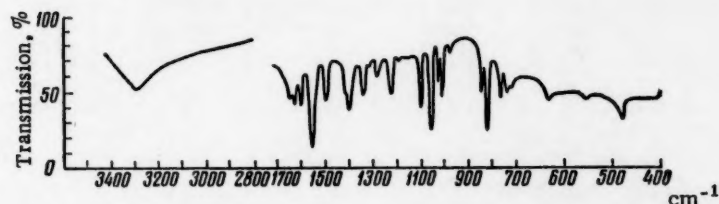


Fig. 4. Infrared absorption spectrum of form I, p-chlorobenznitrolic acid in the region 400-1700 and 2800-3600 cm^{-1} .

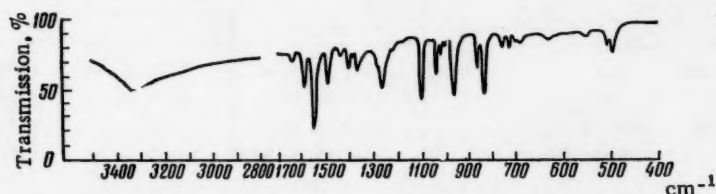


Fig. 5. Infrared absorption spectrum of form II, p-chlorobenznitrolic acid in the region 400-1700 and 2800-3600 cm^{-1} .

hydroxyl and the $\text{C}=\text{N}$ bond (Table 3). A consideration of these frequencies, in which the spectrum of form I of the nitrolic acids corresponded to the spectrum of the anti-nitrolic acids by analogy with the difference in the two isomers of the oximes, showed that, as expected, there was a difference between them in the two forms, of oxime, and the spectrum of form II of the acid agreed with the spectrum of the syn-oxime. In fact, the oscillation of the hydroxyl in the anti-oxime and form I of the nitrolic acids gave a wider absorption band than did the syn-oxime and form III of the acids.

TABLE 2. Infrared Absorption Spectra of Syn- and Anti-p-chlorobenzaldoximes, Forms I and II of p-Chlorobenznitrolic Acids, and p-Chlorophenylnitronitrosomethane in Solid Form in the Region 400-1700 cm^{-1}

Syn-p-chlorobenzaldoxime, cm^{-1}	Anti-p-chlorobenzaldoxime, cm^{-1}	p-Chlorobenznitrolic acids		p-Chlorophenyl-nitronitrosomethane
		Form I, cm^{-1}	Form II, cm^{-1}	
465 m	463 s	480 s	499 m	424 m
498 s	567 s	555 m	508 w	449 w
511 s	595 s	630 s	552 w	484 w
630 w	604 s	720 m	630 w	510 w
700 m	630 m	735 m	690 w	587 w
827 s	710 m	762 m	700 w	632 vw
833 s	760 m	820 vs	723 w	686 m
879 s	821 vs	838 m	750 w	713 m
940 s	870 s	968 w	831 m	752 s
960 s	902 vs	1007 s	859 m	780 m
978 s	960 s	1020 s	958 s	820 m
1015 m	1018 s	1053 vs	991 w	838 m
1038 w	1033 w	1098 s	1013 m	863 m
1091 s	1091 vs	1193 s	1030 m	902 w
1110 m	1110 m	1220 s	1096 s	977 m
1126 w	1190 m	1280 m	1219 w	1004 m
1180 w	1278 m	1312 m	1262 m	1019 m
1206 m	1308 m	1338 s	1280 sh, m	1049 m
1220 w	1344 s	1397 s	1367 m	1092 s
1278 m	1363 m	1410 sh, s	1384 w	1181 m
1305 m	1405 s	1494 s	1404 m	1229 vs
1323 s	1448 s	1552 vs	1435 w	1287 m
1405 m	1491 s	1602 s	1493 m	1316 sh, m
1450 m	1598 s	1628 s	1551 vs	1353 m
1500 s	1628 s	1645 s	1595 m	1376 s
1580 m	1657 s		1645 m	1411 m
1602 m				1551 s
1659 w				1580 vs
				1597 sh, m

TABLE 3. Valence Oscillation Frequencies of Hydroxyl and C=N Bonds of Syn- and Anti-p-chlorobenzaldoxime and Forms I and II of p-Chlorobenznitrolic Acid in Solid Form

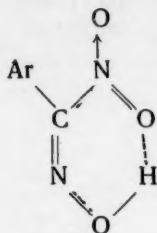
Substance		Valence oscillation of hydroxyl, cm^{-1}		Valence oscillation of C=N bond, cm^{-1}	
		our results	[5]	our data	[6]
p-Chlorobenzaldoxime	syn	3300 m, v. wi	3260 m, wi	1659 w	1650 m
	anti	3170 m, wi	3110 m, wi	1657 s	1645 m
p-Chlorobenznitrolic acid Form I		3290 m, wi		1645 s	
Form II		3340 m, v. wi		1645 m	

* wi, wide; v. wi, very wide.

Moreover, the absorption bands of oscillation of the C=N bonds in the anti-oxime and form I of the nitrolic acid had greater intensity than in the spectra corresponding to the syn-oxime and form II of the acid. Also, in the first pair of substances in this region there was a supplementary frequency of 1628 cm^{-1} which was absent in the second pair of substances. These results indicate that in forms I and II of nitrolic acids there is actually syn-anti isomerism. However, on the basis of spectroscopic data alone it is impossible to speak with certainty as to which of the two forms of nitrolic acid has the syn configuration which the anti. Actually, the close similarity of the spectra, for example, of form I of the nitrolic acid and the anti-oxime still does not mean that in form I the aromatic residue and hydroxyl should be arranged in the same way as in the oxime, on one side of the double bond, since

a priori the possibility is not excluded that in this case the similarity of the spectra depends on the position of the nitro group and not that of the aromatic residue on one side with the hydroxyl group in respect to the double bond.

In seeking another path to establish the configuration of the nitrolic acids we turned our attention to the fact that the syn-configuration of the nitrolic acids should favor the formation of intramolecular hydrogen bonds between the hydrogen of the hydroxyl groups and the oxygen of the nitro groups



since in the anti-configuration the possibility of formation of such bonds is excluded. In the literature there are suggestions of the presence of intramolecular hydrogen bonds in aliphatic nitrolic acids (based on spectral data [2]).

It is known that the participation of the hydroxyl in the formation of intramolecular hydrogen bonds decreases their activity (for example, the acidity of o-hydroxyacetophenone is much less than the acidity of p-hydroxyacetophenone [7]). We decided to take advantage of these properties for showing intramolecular hydrogen bonds which would be shown in the presence of the syn-configuration. For this purpose we studied the acidity of the two forms of p-chlorobenznitrolic acid. In potentiometric titration of solutions of these two substances in 50% aqueous alcohol we found that near pH 5.5 for form II and near pH 7.5 for form I there was initiation of decomposition (accompanied by formation of a precipitate), in view of which we could not obtain a complete titration curve. However, in the beginning part of the titration curve, decomposition had still not occurred; special experiments showed that the forward and reverse course of the titration curves agreed completely up to neutralization of one fourth of the amount of nitrolic acids taken for titration. In this portion of the curves we could obtain a satisfactory estimate of the dissociation constants of both substances. For form I of p-chlorobenznitrolic acid, $pK \approx 7.7$, for form II, $pK \approx 6.1$. Also, the pH of the solutions of the same concentration of the two forms of p-chlorobenznitrolic acid in 50% aqueous alcohol was notably different: for form I pH 5.25, and for form II, pH 4.3.

It is clear from these results that form II of p-chlorobenznitrolic acid is an appreciably more acid substance than form I. Thus, in form I of p-chlorobenznitrolic acid the hydroxyl group takes part in the formation of an intramolecular hydrogen bond, and hence the first form of the arylnitrolic acids can be assigned the syn-configuration, and the second form, the anti-configuration.

The following observation also leads to this conclusion. From a consideration of the model of Stewart-Brigleb, for the syn- and anti-configurations of benznitrolic acid it is evident that in the anti-configuration free rotation around the bond which joins the side chain to the nucleus is difficult, while in the case of the syn-configuration there is no hindrance to free rotation. If we introduce any sort of substituent into the ortho position of the benznitrolic acids, for example, the nitro group, then in the anti-configuration free rotation becomes impossible. Therefore, in chemical reactions of the two possible configurations, there should predominate the formation of the nitrolic acid with the syn-configuration. Actually, in the action of N_2O_4 on p-chlorobenzaldoxime, form I of p-chlorobenznitrolic acid is formed in greater yield than is form II, and when N_2O_4 acts on o-nitrobenzaldoxime, only form I of o-nitrobenznitrolic acid is formed [1]. Thus, again we have found the syn-configuration for form I and the anti-configuration for form II in the nitrolic acids.

SUMMARY

1. We have discovered syn-anti-isomerism in the arylnitrolic acids.
2. Form I of the arylnitrolic acids has the syn-configuration, and form II the anti-configuration.
3. We have confirmed spectroscopically the chemical structure of both forms of arylnitrolic acids, and also of p-chlorophenylnitronitrosomethane.

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MOLECULAR ABSORPTION SPECTRA OF α -HALONITROALKANES

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The absorption spectra of halonitroalkanes were described in a number of publications [1-6], but the data obtained were not correlated or summarized.

In the present work we set ourselves the task of systematically investigating the infrared and ultraviolet absorption spectra of α -halonitroalkanes with the purpose of finding correlations between the structures of these compounds and their spectral characteristics.

Infrared absorption spectra. Consideration of data published in the literature indicates that substitution of an α -hydrogen atom in nitro compounds with halogen (chlorine or bromine) results in a shift of the antisymmetric valency vibration of the NO_2 group towards higher frequencies and a shift of the symmetric valency vibration to lower frequencies [1, 3, 5]. Further accumulation of halogen atoms at the carbon to which the nitro group is attached leads to stronger shift of the frequencies of the antisymmetric and symmetric valency vibrations of the NO_2 group to higher and lower frequencies, respectively [1, 3, 4]. The frequency values of the antisymmetric and symmetric vibrations of the NO_2 group in α -halo nitro compounds depend on the number and disposition of the nitro groups, the aggregate state of the nitro compound being investigated, and the nature of the solvent. The size of the substituent group has no effect on the location of these frequencies in the spectrum [3, 7-9]. The infrared absorption spectra of liquid halonitroalkanes were determined by us on an infrared two-beam UR-10 spectrometer. Because the α -halonitroalkanes investigated react with potassium bromide, the spectra were taken in teflon. The thickness of the teflon was $5\ \mu$. The spectra of the teflon itself, at a thickness of this material amounting to $12\ \mu$, with and without compensation, are shown in Figure 1. As can be seen in Figure 1, teflon is quite suitable for taking spectra in the ranges of 700-1100 and 1260-1700 cm^{-1} .

The spectra of α -halonitroalkanes are shown in Figure 2. The frequencies of the valency vibrations of the nitro group for these compounds are listed in Table 1; data published in the literature on the infrared spectra of α -halonitroalkanes and unsubstituted nitroalkanes are also listed in this Table.

The spectra of all α -halonitroalkanes listed in Table 1 were determined on substances that were in the liquid state; in this manner, the effect of the solvent could be eliminated.

On the basis of the data obtained, we determined the relation between the effective electronegativity* of the α -carbon atom and the change in the frequency of the antisymmetric valency vibration of the NO_2 group. This relation can be expressed by a straight line (Fig. 3) which corresponds to the equation

$$\nu = \nu_0 + \alpha \chi_{\text{eff}}, \quad (1)$$

where ν is the frequency of the NO_2 group; ν_0 and α are constants; and χ_{eff} is the effective electronegativity of the α -carbon atom.

* χ_{eff} , the effective electronegativity of the group $-\text{C} \begin{smallmatrix} \text{X} \\ \diagup \\ \text{Y} \\ \diagdown \\ \text{Z} \end{smallmatrix}$ where X, Y, and Z are hydrogen or halogen atoms, was calculated from the following formula proposed by Kagarize $= \frac{\chi_{\text{C}}}{2} + \frac{1}{6}(\chi_{\text{X}} + \chi_{\text{Y}} + \chi_{\text{Z}})$, in such a manner that this formula was extended by us to cover the case when an aliphatic radical forms one of the substituents. The electronegativity of the radicals beginning with C_2H_5 was assumed to be equal to 2.0 [10], while the electronegativity of the remaining atoms and groups had been assigned values taken from the publications [11].

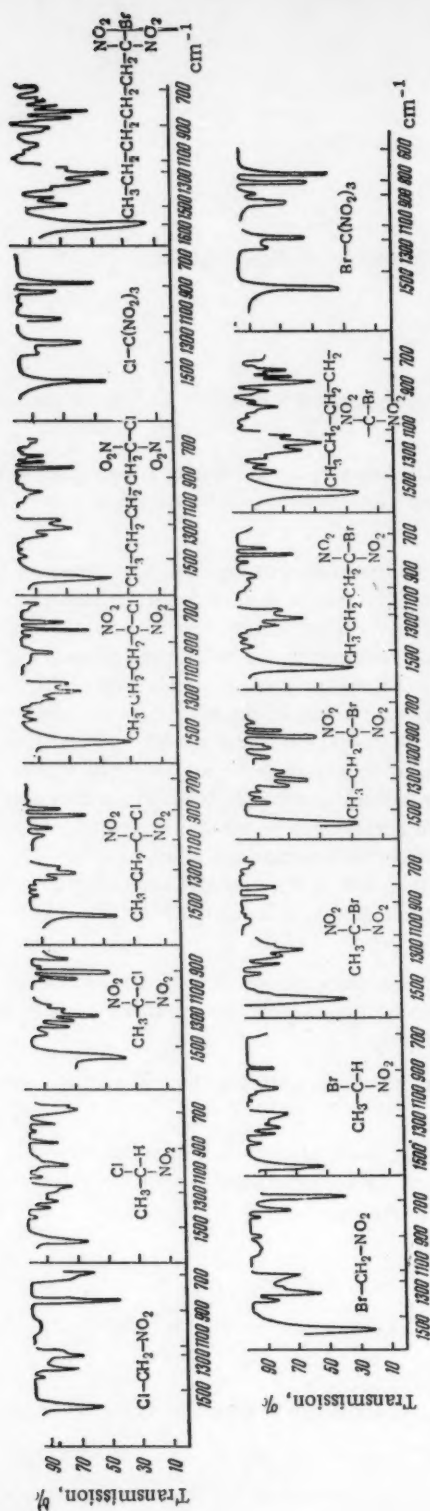


Fig. 2. Infrared absorption spectra of α -halonitroalkanes in the ranges of 700-1100 and 1260-1700 cm^{-1}

The constants ν_0 and α were determined by the method of the least squares. The final form of the equation is

$$\nu = 1311 + 104X_{\text{eff}} \quad (2)$$

The next to last column of Table 1 lists values of frequencies calculated from this equation while the last column indicates deviations of the calculated values from values found experimentally. These deviations are very small—in other words, there is close correspondence to the rectilinear relation described by equation (2). One may therefore conclude that the principal factor which determines the frequency of the antisymmetric valency vibration of the NO_2 group is the electronic state expressed in the so-called electronegativity of the α -carbon atom, which exerts an effect on the change of the force constant of the N-O bond. Daasch [12] pointed out that there is a rectilinear relation between the electronegativity of the α -carbon atom and the frequency of the antisymmetric valency vibration of the NO_2 group. However, the limited number of objects of experimentation cited in Daasch's work [12] and the failure to maintain standard conditions in the determination of spectra made it impossible to establish whether or not the relationship found has general validity.

As a result of our work, which has been carried out on a great number of experimental objects and conducted under rigidly standardized conditions, it was possible to establish that the existence of a regularly occurring correlation between the determined effective electronegativity of the α -carbon atom and the frequency of the antisymmetric valency vibration of the NO_2 group is a generally encountered phenomenon.

Consideration of the frequencies of the symmetric valency vibrations of the NO_2 group indicates that these frequencies are the same for every pair of compounds which have the same constitution but differ only as far as the halogen atom (chlorine or bromine) is concerned, although

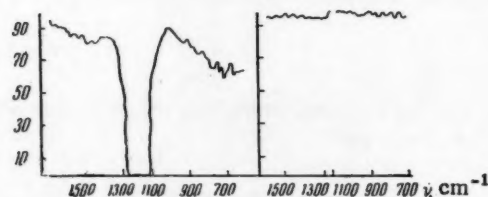


Fig. 1. Infrared absorption spectra of teflon at a thickness of 12 μ : a) Without compensation; b) with compensation.

TABLE 1. Valency Vibrations of the NO₂ Groups in α -Halonitroalkanes and Nitroalkanes

Order No.	Formula	Name of compound	Valency vibrations of the NO ₂ gp in cm ⁻¹		χ_{eff}	$\nu_{\text{antisymm. calculated}}$	$\Delta \nu = \nu_{\text{exp}} - \nu_{\text{calc.}}$
			sym-metric	anti-sym-metric			
1	CH ₃ BrNO ₂	Bromonitromethane	1369	1570	2,44	1565	+5
2	CBr ₃ NO ₂	Tribromonitromethane	1307	1595	2,65	1587	+8
3	CH ₃ ClNO ₂	Chloronitromethane	1368	1578	2,48	1571	+7
4	CCl ₃ NO ₂	Trichloronitromethane	1307	1610	2,76	1598	+12
5	CH ₃ CHBrNO ₂	1-Bromo-1-nitroethane	1354	1570	2,48	1571	-1
6	CH ₃ CHClNO ₂	1-Chloro-1-nitroethane	1356	1575	2,52	1573	+2
7	CH ₃ CCl ₂ NO ₂	1,1-Dichloro-1-nitroethane	1348	1570	2,52	1573	-3
8	CH ₃ CBr(NO ₂) ₂	1-Bromo-1,1-dinitroethane	1325	1587	2,66	1588	-1
9	CH ₃ CCl(NO ₂) ₂	1-Chloro-1,1-dinitroethane	[3]	[3]	2,70	1592	-5
10	CH ₃ CH ₂ CBr(NO ₂) ₂	1-Bromo-1,1-dinitropropane	1315	1587	2,74	1596	-7
11	CH ₃ CH ₂ CCl(NO ₂) ₂	1-Chloro-1,1-dinitropropane	1314	1589	2,64	1586	-3
12	CH ₃ CH ₂ CH ₂ CBr(NO ₂) ₂	1-Bromo-1,1-dinitrobutane	1309	1583	2,68	1590	-3
13	CH ₃ CH ₂ CH ₂ CCl(NO ₂) ₂	1-Chloro-1,1-dinitrobutane	1312	1587	2,64	1586	0
14	CH ₃ (CH ₂) ₃ CHBrNO ₂	1-Bromo-1-nitropentane	1314	1589	2,68	1590	-1
15	CH ₃ CH ₂ CH ₂ CH ₂ CBr(NO ₂) ₂	1-Bromo-1,1-dinitropentane	1350	1567	2,42	1563	+4
16	CH ₃ CH ₂ CH ₂ CH ₂ CCl(NO ₂) ₂	1-Chloro-1,1-dinitropentane	[5]	[5]	2,64	1586	-1
17	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CBr(NO ₂) ₂	1-Bromo-1,1-dinitrohexane	1313	1585	2,68	1590	0
18	BrC(NO ₂) ₃	Bromotrinitromethane	1315	1590	2,64	1586	0
19	ClC(NO ₂) ₃	Chlorotrinitromethane	1293	1609	2,88	1611	-2
20	RCH ₂ NO ₂	Primary nitroalkanes	1281	1617	2,92	1615	+2
21	RR ₁ CHNO ₂	Secondary nitroalkanes	1382	1554	2,32	1552	+2
22	RR ₁ R ₂ CNO ₂	Tertiary nitroalkanes	[7]	[7]	2,30	1550	0
23	RCH(NO ₂) ₂	1,1-Dinitroalkanes	1360	1550	2,28	1548	-10
24	HC(NO ₂) ₃	Trinitromethane	[7]	[7]	2,54	1575	0
25	RC(NO ₂) ₃	1,1,1-Trinitroalkanes	1348	1538	2,78	1600	-3
26	C(NO ₂) ₄	Tetranitromethane	1333	1575	2,76	1598	+2
			[7]	[7]			
			1266	1618	3,00	1623	-5
			[2]	[2]			

it would seem that these frequencies must be lower for the more strongly electronegative chlorine atom. One must assume that the steric factor or the mass of the bromine atom begins to have an effect, or that perhaps both of these factors are effective. Both factors may lower the frequency of the symmetric valency vibration of NO₂ group of α -bromonitroalkanes to a value which corresponds to the frequency of an α -chloronitroalkane.

Ultraviolet absorption spectra. Rather meager information is available in the literature [1, 2, 6] on the ultraviolet absorption spectra of α -halonitroalkanes. Introduction into the α -position with reference to the nitro group of an auxochrome, i.e., a chlorine atom, exerts a small and varying bathochromic effect. The effect of the solvent is also not great. Massing of a greater number of chlorine atoms at the α -carbon atom was found to have the effect

TABLE 2. Ultraviolet Absorption Spectra of α -Halonitroalkanes in Isooctane

Order No.	Formula	Name of compound	Maximum		$\Delta\epsilon = \epsilon_{\max} - \epsilon'_{\max}$ *	Minimum	
			$\lambda, m\mu$	ϵ		$\lambda, m\mu$	ϵ
1	CH_3CINO_2	Chloronitromethane	276 w	26	1	246 w	13
2	$\text{CH}_3\text{CHCINO}_2$	1-Chloro-1-nitroethane	282 w	29	4	248 w	14
3	$\text{CH}_3\text{CCl}(\text{NO}_2)_2$	1-Chloro-1,1-dinitroethane	281 w	75	17	251 w	37
4	$\text{CH}_3\text{CH}_2\text{CCl}(\text{NO}_2)_2$	1-Chloro-1,1-dinitropropane	280 w	78	20	251 w	42
5	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CCl}(\text{NO}_2)_2$	1-Chloro-1,1-dinitrobutane	280 w	84	26	251 w	43
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CCl}(\text{NO}_2)_2$	1-Chloro-1,1-dinitropentane	279 w	81	23	251 w	41
7	$\text{ClC}(\text{NO}_2)_3$	Chlorotrinitromethane	277 w	129	31	268 w	121
8	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{Cl} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1-Chloro-1,1,3,3-tetranitrobutane	280 w	160	19	260 w	128
9	$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{Cl} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1-Chloro-1,1,3,3-tetranitropentane	279 w	160	19	258 w	118
10	$\begin{array}{c} \text{Cl}-\text{C}-\text{C}-\text{Cl} \\ \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1,2-Dichloro-1,1,2,2-tetranitroethane	269 inf.	215	64	—	—
11	$\begin{array}{c} \text{Cl}-\text{C}-\text{CH}_2-\text{C}-\text{Cl} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1,3-Dichloro-1,1,3,3-tetranitropropane	277 w	194	53	260	174
12	CH_3BrNO_2	Bromonitromethane	282 w	44	19	270 w	42
13	$\text{CH}_3\text{CHBrNO}_2$	1-Bromo-1-nitroethane	284 w	57	22	272 w	55
14	$\text{CH}_3\text{CBr}(\text{NO}_2)_2$	1-Bromo-1,1-dinitroethane	280 w	108	50	268 w	105
15	$\text{CH}_3\text{CH}_2\text{CBr}(\text{NO}_2)_2$	1-Bromo-1,1-dinitropropane	289 w	106	48	269 w	96
16	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CBr}(\text{NO}_2)_2$	1-Bromo-1,1-dinitrobutane	277 w	125	67	270 w	123
17	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CBr}(\text{NO}_2)_2$	1-Bromo-1,1-dinitropentane	279 w	112	54	268 w	110
18	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CBr}(\text{NO}_2)_2$	1-Bromo-1,1-dinitrohexane	277 w	113	55	269 w	111
19	$\text{BrC}(\text{NO}_2)_3$	Bromotrinitromethane	~278 w inf	180	82	—	—
20	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{Br} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1-Bromo-1,1,3,3-tetranitrobutane	275 w	185	44	268 w	180
21	$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{Br} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1-Bromo-1,1,3,3-tetranitropentane	277 w	185	44	265 w	178
22	$\begin{array}{c} \text{Br}-\text{C}-\text{CH}_2-\text{C}-\text{Br} \\ \quad \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array}$	1,3-Dibromo-1,1,3,3-tetranitropropane	~274 w inf	235	94	—	—

* This column lists values of $\Delta\epsilon$ which represents the difference between the intensities of maxima in the spectra of halo-dinitroalkanes and those of the corresponding nitroalkanes.

The values of ϵ_{\max} for mono-, di-, tri-, and tetranitroalkanes are taken from the publications [7, 15].

of shifting the maximum of absorption towards shorter wave lengths. In addition to that, one may conclude on the basis of data available in the literature that introduction of a halogen atom (chlorine) at the α -carbon atom results in an increase of the magnitude of the coefficient of extinction in such a manner that this phenomenon becomes more pronounced as the number of halogen atoms at the α -carbon increases. Introduction of three halogen atoms (bromine) into nitromethane leads to a sharp increase of the coefficient of extinction ($\epsilon_{280} = 400$) and to a disappearance of the maximum of absorption, which is ascribed to the spatial effect of the three bromine atoms on the nitro groups [1]. Bromine exerts the same effect in β -halo- β -nitro alcohols [6].

We determined the ultraviolet absorption spectra of α -halonitroalkanes on an SF-4 spectrophotometer using solutions in isooctane; the concentrations were in the range of 0.75-2.0 g/l. The extinction coefficient, ϵ , was calculated from the formula $\epsilon = D/c \cdot l$, where D is the optical density, c the concentration in moles per liter, and l the thickness of the layer in cm. The data obtained are listed in Table 2.

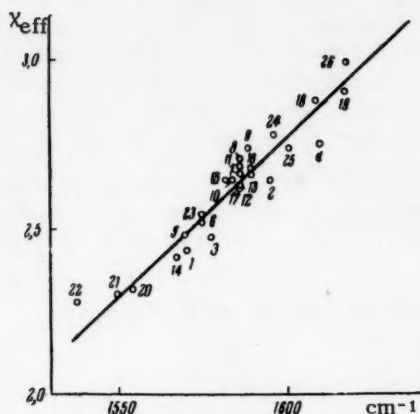


Fig. 3. Dependence of the frequency of the antisymmetric valency vibration of the NO_2 group on the effective electronegativity of the α -carbon atom (the numbers of the points plotted correspond to the order numbers of the substances in Table 1).

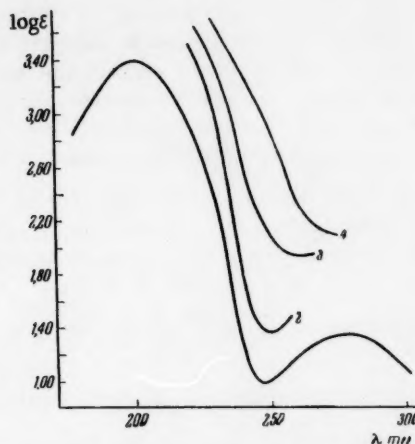


Fig. 4. Displacement of λ_{\min} into the long-wave range with the accumulation of nitro groups in nitroalkanes: 1) Nitromethane; 2) dinitroethane; 3) trinitroethane; 4) tetra-nitromethane.

It is known that the nitro group in saturated aliphatic nitro compounds exhibits 2 absorption bands, at $\sim 210^\circ$ and $280 \text{ m}\mu$ [13]. The first of these bands is correlated with the electronic transition $\text{N} \rightarrow \text{V}$ and the second with the forbidden transition $\text{N} \rightarrow \text{Q}$. The first band has an intensity which is many times greater than that of the second band. Unfortunately, by using an SF-4 spectrophotometer, one can measure only the band in the region of the longer waves, i.e., that at $\sim 280 \text{ m}\mu$, and cannot measure the band at $\sim 210 \text{ m}\mu$, which lies in the region of vacuum ultraviolet.

The data accumulated by us in the present work and preceding investigations [7] and also the data published in the literature in regard to spectra of aliphatic nitro compounds [1, 2, 6] indicate that one must exercise caution in evaluating the long-wave ($280 \text{ m}\mu$) band in spectra of aliphatic nitro compounds. Because this band is very wide, one cannot tell with precision just where the maximum is located.

The smoothing out of the maximum of this band (appearance of an inflection at $\sim 280 \text{ m}\mu$ instead of a clear maximum and minimum), which is observed with the increase of the coefficient of extinction in spectra of α -halonitroalkanes [1, 9] and also in the spectra of nitroamines and nitrodiols [13] presumably cannot be explained without taking into consideration the behavior of the more intense band at $\sim 210 \text{ m}\mu$.

Attempts to explain the smoothing out of the maximum referred to above by a steric effect of the bromine (in α -halonitroalkanes [1, 9]) or to the formation of a hydrogen bond (in nitroamines and nitroalcohols [14]) appear ill-founded to us.

The effect of the 210 m μ band on the 280 m μ band can be illustrated by data determined in the present work. Chloronitromethane and 1-chloro-1-nitroethane (c.f., Table 2) which contained only one nitro group each, have a λ_{\min} at ~ 245 m μ ($\epsilon = 15$ units) and a λ_{\max} at ~ 280 m μ (ϵ_{\max} 26 and 29 units, respectively) which is characteristic for a nitro group in ordinary mononitroalkanes [7].

The remaining 17 compounds (c.f. Table 2) have a λ_{\min} that is displaced into the region of longer waves and also larger coefficient of extinction of the minimum, with these phenomena expressed more strongly in the case of bromo derivatives than that of chloro derivatives. These substances do not exhibit a minimum at all, but only an inflection of the curve.

This shift of λ_{\min} and increase in the value of ϵ_{\min} or even complete disappearance of the minimum can be explained by assuming that the cause of this phenomenon is a change in the band at ~ 210 m μ , a band which has not been investigated yet. The change may consist either in an increase of the intensity of this band with a corresponding increase of its width or a shift of the band into the region of longer waves.

In connection with the investigation of the effect of the band at ~ 210 m μ on the position of the band at ~ 280 m μ in the spectra of nitro compounds, the spectra of some nitroalkanes in the range of 170-240 m μ (vacuum ultraviolet) were studied in the present work. It was established that with the accumulation of NO₂ groups in nitroalkanes (from nitromethane to dinitroethane, trinitroethane, and tetranitromethane—c.f. Fig. 4*) the intensity of the band at ~ 210 m μ increases and the band widens which brings about a shift of λ_{\min} into the longer wave range and an increase in the coefficient of extinction of the maximum of the band at ~ 280 m μ .

The correctness of the assumption in regard to the effect of the band at ~ 210 m μ is confirmed by the fact that an atom of chlorine or bromine increases the ϵ_{\max} in tetranitroalkanes by approximately the same value as in heminal dinitroalkanes. The presence of two chlorine or bromine atoms multiplies this increment by a factor of ~ 2 (c.f. Table 2).

The authors express their thanks to G. K. Klimenko for putting at their disposal an UR-10 apparatus.

SUMMARY

1. The molecular absorption spectra of 22 α -halonitroalkanes were investigated.
2. It was found that the principal factor which exerts an influence on the antisymmetric valency vibrations of the NO₂ groups in infrared spectra is the effective electronegativity of the α -carbon atom.
3. It follows from data obtained by the investigation of ultraviolet spectra that one must exercise caution in interpreting the behavior of the band ~ 280 m μ , because in spectra of saturated aliphatic nitro compounds changes in the band at ~ 210 m μ may affect this behavior.

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* These data were obtained in P. P. Shorygin and V. A. Petukhov's laboratory by using a vacuum spectrophotometer.

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CONDENSATION OF CYCLOPENTADIENE WITH MONO- AND DISUBSTITUTED NITROOLEFINS

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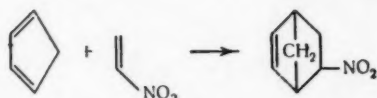
Translated from Doklady Akademii Nauk, Otdelenie Khimicheskikh Nauk,

No. 4, pp. 690-695, April, 1961

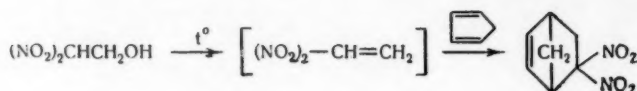
Original article submitted March 3, 1960

We have previously [1] carried out condensation of hexachlorocyclopentadiene with mono- and 1,2-disubstituted nitroolefins and have shown that the former react with the diene forming adducts in good yields, and that the disubstituted compounds do not give adducts with hexachlorocyclopentadiene even on heating for 30 hours.

In this work we studied the reaction of cyclopentadiene with monosubstituted ethylenes (nitroethylene and nitroallyl), 1,2-disubstituted ethylenes (β -nitrostyrene, β -nitroacrylic acid, its methyl ester and nitrile, and β -trichloromethylnitroethylene), and 1,1-dinitroethylene. As would be expected and as seen from the data in the literature [2], nitroethylene reacts smoothly with cyclopentadiene even at 0°, giving an adduct in 73% yield.

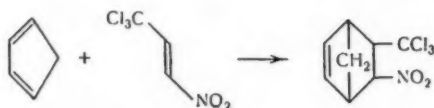


In contrast to 2-nitroalkenes-1, which can be regarded as 1,1-disubstituted phylodienes and which condense with cyclopentadiene with great difficulty [3, 4], 1,1-dinitroethylene (formed by dehydrating 1,1-dinitroethanol-2 under the reaction conditions) gives an adduct in 65% yield with cyclopentadiene on boiling for 15-20 minutes in chlorobenzene



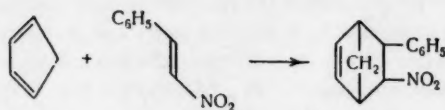
The cause of this different behavior of phylodienes of the same type must evidently be sought in the nature of the substituents: if in 2-nitroalkenes-1 and NO₂ and an alkyl-group are attached to the same carbon atom and the latter group partially "extinguishes" the activating effect of the nitro-group exerted on the double bond, then in 1,1-dinitroethylene both substituents are of the same nature and exert a "coordinated" effect.

We have not observed 1,1-dinitroethanol-2 in special detail, as this has been done by Gold, Hammel, and Klager [5], but have obtained the direct condensation product of dinitromethane with formaldehyde [6]. On comparing the experimental results of condensing cyclopentadiene with 1,2-disubstituted phylodienes: β -nitrostyrene, β -nitroacrylic acid, its nitrile and methyl ester, and β -trichloromethylnitroethylene, we noticed the fact that the latter reacts with much greater difficulty than the remaining phylodienes of this type. To obtain a high yield (86%) of adduct it is necessary to boil the mixture of diene and phylodiene in benzene for 17 hours.



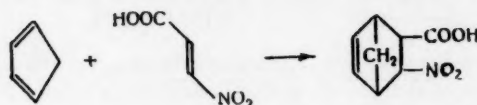
On carrying out the reaction under the conditions used by us in condensing cyclopentadiene with β -nitrostyrene and β -nitroacrylic acid (boiling in benzene for 5 hours), the adduct was formed in lower yield (~60%).

The lower reactivity of β -trichloromethylnitroethylene evidently results from steric hindrance caused by the presence of trichloromethyl group. Under the same conditions, β -nitrostyrene condenses practically quantitatively with cyclopentadiene on heating the components on a boiling water bath for 5 hours. In this case, steric hindrance plays a lesser part, because of as a result of the planar structure of the benzene ring and its free rotation around the C-C bond, while electronic factors begin to play a considerably greater part,

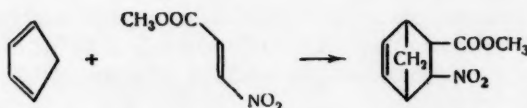


β -Nitroacrylic acid, its nitrile and methyl ester, react vigorously with cyclopentadiene. This evidently is a result of the activating effect exerted on the double bond by the two electronegative groups of the phylodiene.

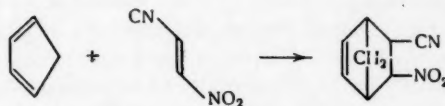
Thus, on boiling a mixture of β -nitroacrylic acid and cyclopentadiene in benzene for 5 hours, a bicyclic acid is formed in 90% yield.



The methyl ester of the latter was obtained in 43% yield by reacting the methyl ester of β -nitroacrylic acid with cyclopentadiene.

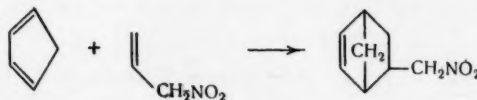


The nitrile of β -nitroacrylic acid reacts vigorously on mixing it with cyclopentadiene in benzene at 20°, but the adduct is formed in low yield (~25%). A similar low yield of this adduct (24%) was also obtained on heating the nitrile of β -nitroacrylic acid with cyclopentadiene in benzene at 80° for 5 hours.



The low yields of adducts from the nitrile and methyl ester of β -nitroacrylic acid are evidently related to the low stability of the initial phylodienes [7].

In nitroallyl the double bond is very weakly activated by the nitro group situated in the β -position, and thus it condenses with cyclopentadiene with much greater difficulty; on heating a mixture of nitroallyl and cyclopentadiene in chlorobenzene at 130-150° for 9 hours, an adduct was obtained in 24% yield.



EXPERIMENTAL

Condensation of Cyclopentadiene with Nitroethylene. To a solution of 82.5 g (1.26 M) of cyclopentadiene in 100 ml of absolute benzene with addition of pyrogallol was added dropwise a solution of 18.45 g (0.253 M) of nitroethylene in 100 ml of absolute benzene at a temperature of 0° over a period of 1 hour. The mixture was allowed

to stand overnight at room temperature, the solvent evaporated off and the residue distilled. 25.2 g (73% theoretical) of 2-nitrobicyclo(2,2,1)-heptene-5 was obtained with b.p. 104-109° (12-14 mm); it solidified at room temperature. Data in the literature [2]: 92-94° (8 mm).

Condensation of Cyclopentadiene with Nitroallyl. To obtain nitroallyl, to a solution of 72 g (0.5 M) of freshly distilled allyl bromide in 120 ml of hexane was added without delay 83 g (0.54 M) of silver nitrite at room temperature. After several minutes the temperature of the reaction mixture was raised to the boiling point of the solvent. To avoid losing the reaction mixture, cooling it with ice water was necessary. The reaction mixture was then cooled to 40° and stirred at the temperature for 3 hours. The precipitate was filtered off, and hexane distilled off under weak vacuum (40 mm Hg) at room temperature. 22 g of nitroallyl was obtained with b.p. 42° (24 mm). Data in the literature [8]: b.p. 87-89° (180 mm); 125-130° (760 mm).

To prepare 2-nitromethylbicyclo(2,2,1)heptene-5, a solution of 2.7 g (0.03 M) of freshly distilled nitroallyl [b.p. 37° (20 mm)] and 3.96 g (0.06 M) of freshly distilled cyclopentadiene in 10 ml of chlorobenzene was boiled under reflux condenser for 7 hours; pyrogallol was added to prevent polymerization. After completion of the reaction, chlorobenzene and unreacted cyclopentadiene and nitroallyl were distilled off under the vacuum of a water-jet pump. The residue was distilled in a stream of nitrogen. 1.1 g (24% theoretical) of 2-nitromethylbicyclo(2,2,1)heptene-5 was obtained with b.p. 102° (8 mm); 92° (4 mm); n_D^{20} 1.4953; d_4^{20} 1.1253. Found: C 63.00; 63.07; H 7.16; 7.04; N 9.11; 9.37%. $C_8H_{11}NO_2$. Calculated: C 62.74; H 7.18; N 9.15%.

Condensation of Cyclopentadiene with 1,1-Dinitroethylene. For the reaction we took not 1,1-dinitroethylene, but 1,1-dinitroethanol-2, which, as is known, is readily dehydrated under condensation conditions [5]. 1,1-Dinitroethanol was prepared as described in an article by Duden and Pondorf [6]. To a boiling solution of 9.8 g (0.148 M) of cyclopentadiene (freshly distilled) in 15 ml of chlorobenzene was added dropwise over a period of 10 minutes to a solution of 7.4 g (0.054 M) of 1,1-dinitroethanol-2 in 30 ml of chlorobenzene, and then stirred at boiling point for 20 minutes. The solution was stirred with activated carbon at 40° for 30-40 minutes, filtered from the carbon, and chlorobenzene removed in vacuo; the residue crystallized on cooling. Yield of technical 2,2-dinitrobicyclo(2,2,1)-heptene-5 was 6.9 g (65% theoretical), m.p. 117-118° [subliming at 145° (2-3 mm)]. Data in the literature: m.p. 117-118° [5]. Found: C 45.41; 45.34; H 4.47; 4.45%. $C_7H_8N_2O_4$. Calculated: C 45.65; H 4.34%.

Condensation of β -Nitrostyrene with Cyclopentadiene. A mixture of 7.95 g (0.05 M) of β -nitrostyrene and 6.6 g (0.1 M) of freshly distilled cyclopentadiene with addition of pyrogallol was heated on a boiling water bath for 5 hours with reflux condenser and distilled. 10.8 g (96% theoretical) of 2-nitro-3-phenylbicyclo(2,2,1)heptene-5 was obtained with b.p. 142-145° (1-2 mm); n_D^{20} 1.5640; data in the literature [9, 10]: 145° (1 mm); n_D^{20} 1.5641.

Condensation of Cyclopentadiene with β -Nitroacrylic Acid. β -Nitroacrylic acid, its methyl ester and nitrile were prepared by the method described previously [7]. To a solution of 1.2 g (0.02 M) of freshly distilled cyclopentadiene in 5 ml of absolute benzene was added dropwise a solution of 2.34 g (0.02 M) of β -nitroacrylic acid in 10 ml of absolute benzene in presence of inhibitor. The temperature was then lowered to 32°. The solution was boiled for 5 hours, and benzene evaporated off; the residue crystallized on cooling. 3.2 g (90.5% theoretical) of 2-nitro-3-carboxybicyclo(2,2,1)heptene-5 was obtained with m.p. 95-96° (from hexene). Found: C 52.85; 52.66; H 5.24; 5.27; N 7.64; 7.69%. $C_8H_9NO_4$. Calculated: C 52.45; H 4.91; N 7.65%.

Condensation of Cyclopentadiene with the Methyl Ester of β -Nitroacrylic Acid. To a solution of 2 g (0.03 M) of cyclopentadiene in 5 ml of absolute benzene with addition of pyrogallol was added a solution of 3.8 g (0.029 M) of the methyl ester of β -nitroacrylic acid in 2 ml of absolute benzene at room temperature. The mixture was then boiled on a water bath for 5 hours. After solvent evaporation, the residue was distilled in vacuo. 2.45 g (43% theoretical) of 2-nitro-3-carbomethoxybicyclo(2,2,1)heptene-5 was obtained with b.p. 106-107° (2 mm); n_D^{20} 1.4912; d_4^{20} 1.2551. Found: C 54.45; 54.44; H 5.68; 5.60; N 7.09; 6.97%. $C_9H_{11}NO_4$. Calculated: C 54.82; H 5.58; N 7.10%.

Condensation of Cyclopentadiene with the Nitrile of β -Nitroacrylic Acid.

Experiment 1. To a solution of 3.96 g (0.06 M) of freshly distilled cyclopentadiene in 6 ml of absolute benzene with pyrogallol addition was added dropwise with stirring at 20° (cooling) 4.25 g (0.04 M) of distilled nitrile of β -nitroacrylic acid. A white, crystalline precipitate then settled out. The reaction mixture was stirred for 2 hours at 20-22°, then for 2 hours at 50-60°; the precipitate was filtered off. 1.6 g (~25% theoretical) of 2-nitro-3-cyanobicyclo(2,2,1)heptene-5 was obtained with m.p. 142-142.5° (from ethyl alcohol). Found: C 58.46; 58.57; H 4.98; 4.96; N 17.01; 17.05%. $C_8H_8N_2O_2$. Calculated: C 58.53; H 4.87; N 17.07%.

Experiment 2. A mixture of 3.5 g (0.036 M) of the nitrile of β -nitroacrylic acid, 3.6 g (0.054 M) of freshly distilled cyclopentadiene, and 15 ml of absolute benzene was boiled under reflux condenser for 5 hours, pyrogallol being added to prevent polymerization. The solvent was evaporated off, the resinous residue crystallizing on standing. 1.4 g (24% theoretical) of 2-nitro-3-cyanobicyclo(2,2,1)heptene-5 was obtained m.p. 142-142.5° (from ethyl alcohol).

Condensation of Cyclopentadiene with β -Trichloromethylnitroethylene. β -Trichloromethylnitroethylene was prepared by the method described in the literature [11].

Experiment 1. A mixture of 5.23 g (0.027 M) of β -trichloromethylnitroethylene, 5 g of freshly distilled cyclopentadiene, 10 ml of absolute benzene, and 1 ml of acetic acid was boiled under reflux condenser for 17 hours in the presence of pyrogallol. After completion of reaction, solvent and unreacted dicyclopentadiene were evaporated off, and the residue distilled. 6.02 g (~86% theoretical) of 2-nitro-3-trichloromethylbicyclo(2,2,1)heptene-5 was obtained with b.p. 120-123° (2 mm); n_D^{20} 1.5342; d_4^{20} 1.4908. Found: C 37.27; 37.56; H 3.07; 3.12; Cl 41.52; 41.32%. $C_8H_6NO_2Cl_3$. Calculated: C 37.13; H 3.08; Cl 41.18%.

Experiment 2. A mixture of 3.9 g (0.02 M) of β -trichloromethylnitroethylene, 2.6 g (0.04 M) of freshly distilled cyclopentadiene, 7 ml of absolute benzene, and 0.5 ml of glacial acetic acid was boiled under reflux condenser for 5 hours in presence of pyrogallol. After reaction completion, solvent and unreacted dicyclopentadiene were evaporated off, and the residue distilled. 3.12 g (~60% theoretical) of 2-nitro-3-trichloromethylbicyclo(2,2,1)-heptene-5 was obtained with b.p. 124-126° (3 mm); n_D^{20} 1.5346.

SUMMARY

1. Condensation was achieved of cyclopentadiene with monosubstituted (nitroethylene and nitroallyl), and 1,1,- and 1,2-disubstituted (1,1-dinitroethylene, nitrostyrene, β -nitroacrylic acid, its nitrile and methyl ester, and β -trichloromethylnitroethylene) nitroolefins.
2. Both the nature of the substituents and their volume affected the reactivity of the nitrophylodiene.
3. For the first time, a series of bicyclic adducts containing functional groups together with a nitro-group was prepared and characterized.

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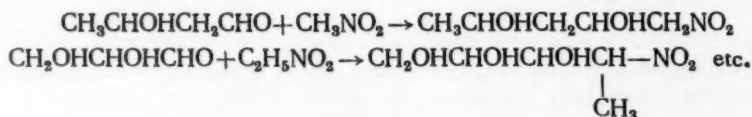
CONDENSATION OF NITROALKANES WITH ACETALDOL

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Original article submitted March 3, 1960

Condensation of mononitroalkanes with various aliphatic aldehydes in presence of alkaline catalysts leads to formation of the corresponding nitroalcohols, nitroglycols, and nitroalkanetriols [1].

We were faced with the problem of investigation condensation of nitroalkanes with hydroxylaldehydes, for instance:



In contrast to condensation of mononitroalkanes with aldehydes, covered quite well in the literature, reaction of nitroalkanes with hydroxylaldehydes has been described only for condensation of nitromethane with glycolic aldehyde [2] and sugars [3]. In the first instance the authors did not isolate the condensation product, but reduced it with aluminum amalgam, decomposed the reduction product by heating with NaNO_2 and obtained glycerin in poor yield as the final product.

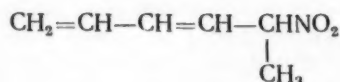
By condensing nitromethane with monoses, polyatomic nitroalcohols corresponding to the initial monoses were obtained and hydrolyzed to the corresponding aldols.

We have studied the reaction of acetaldo1 with CH_3NO_2 in a CH_3OH medium in presence of $\text{Ba}(\text{OH})_2$ at room temperature and obtained a condensation product as a viscous oil which could not be distilled. On treating an ethereal solution of this product with ketene, a mixture of unsaturated monoacetates was formed, which on distillation in presence of small amounts of CH_3COONa gave a mixture of two nitropentadienes, consisting, according to spectral analytical data, of $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CHNO}_2$ (main form) and $\text{CH}_2=\text{CH}-\text{CH}=\text{CHCH}_2\text{NO}_2$. A similar mixture of the nitrodienes shown was formed on distilling the condensation product of nitromethane and acetaldo1 in presence of phthalic anhydride.

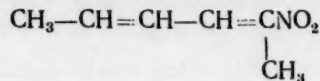
Other methods of dehydrating the diol obtained (distillation with KHSO_4 , $p\text{-C}_7\text{H}_7\text{SO}_3\text{H}$, treatment with P_2O_5 in ether) led to resinification of the reaction mixture, from which diol dehydration products could not be isolated.

Carrying out condensation in presence of other catalysts (K_2CO_3 , NaOH), condensation product yield was lower; using $(\text{CH}_3)_3\text{NH}$ as catalysts, and also attempting to accomplish the condensation indicated via a bisulfite compound, intense resinification was observed.

Reacting acetaldo1 with $\text{C}_2\text{H}_5\text{NO}_2$ in presence of $\text{Ba}(\text{OH})_2$ or NaOH (1 M) a condensation product was also formed as a light-yellow, viscous oil, which on distillation with phthalic anhydride split off water and gave a mixture of nitrohexadienes, consisting, according to spectral analytical data, of



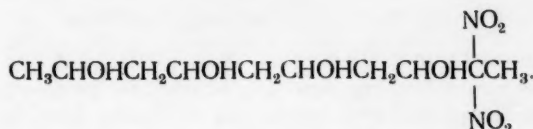
and



Acetylating the condensation product of acetaldo1 with $C_2H_5NO_2$ by means of ketene in ethereal solution, a mixture of acetates was formed, from which an unsaturated acetate was isolated.

Condensation of acetaldol with 2-nitropropane in a CH_3OH medium in presence of $\text{Ba}(\text{OH})_2$ led to formation of a product, dehydration of which by heating with phthalic anhydride gave 2-nitro-2-methylhexadiene-3,5.

Reacting acetaldol with 1,1-dinitroethane in aqueous methanol solution in presence of several drops of H_2SO_4 , 2,2-dinitrodecanetetrol-3,5,7,9 was obtained



This tetrol can also be obtained by reacting the sodium salt of 1,1-dinitroethane with acetaldol in an aqueous medium in presence of CH_3COOH .

Condensing acetaldol with dinitromethane, an unstable oil is formed, decomposing on distillation in vacuo and on storage. Attempts at dehydrating it led to complete resinification. The acetylation product of this oil with ketene on distillation in presence of CH_3COONa and on treatment with KHCO_3 in chloroform solution resinsified intensely, isolation of individual products then being impossible.

EXPERIMENTAL

Condensation of Acetaldo1 with Nitromethane. To a mixture of 10 g of CH_3NO_2 , 25 ml of CH_3OH , and 0.9 g of $\text{Ba}(\text{OH})_2$ was added from a dropping funnel 8.8 g of aldol and the mixture stirred for 4-5 hours at 20° . On the following day it was neutralized with dilute H_2SO_4 , and BaSO_4 , precipitate settling out filtered off, CH_3OH distilled off under low vacuum and the condensation product obtained as a transparent, yellow oil; n_D^{20} 1.4700-1.4720; yield 15-17 g.

Dehydration of Condensation Product of Acetaldo1 with Nitromethane. A mixture of 4 g of oil n_D^{20} 1.4700 and 4 g of phthalic anhydride was heated in a flask with fractionating column under water-jet pump vacuum; at bath temperature 135-150° and 7-8 mm vacuum, water drops appeared on the condenser, and at bath temperature 160-163° a mixture of 1-nitropentadiene-1,3 and 1-nitropentadiene-2,4- distilled off as a mobile, yellow oil with a sharp, lachrymatory odor; yield 1.5 g; b.p. 76-78° (8 mm); n_D^{20} 1.5529; 1645, 1610 cm^{-1} (C=C); 1345, 1515 cm^{-1} and (NO_2). Found: C 52.64; H 6.20; N 11.80%. $\text{C}_8\text{H}_7\text{O}_2\text{N}$. Calculated: C 53.10; H 6.20; N 12.35%.

Acetylation of Condensation Product of Acetaldo1 with Nitromethane. Into an ethereal solution of 15 g of condensation product of 8.8 g of aldol with CH_3NO_2 (see above), n_D^{20} 1.4720, was bubbled with cooling with ice a stream of ketene (10-20% in excess over that theoretically necessary for acetylation of the two hydroxyl groups of the amount of ketene), ether finally evaporated off in vacuo, the residue distilled and a mixture of unsaturated mono-acetates obtained; yield 4.6 g; b.p. $92-93^\circ$ (2 mm); n_D^{20} 1.4460; d_4^{20} 1.1723. Found: C 48.78; H 7.50; N 8.24%. $\text{C}_7\text{H}_{11}\text{O}_4\text{N}$. Calculated: C 48.55; H 6.30; N 8.10%.

Splitting-off of CH_3COOH from Mixture of Unsaturated Acetates of Composition $\text{C}_7\text{H}_{11}\text{O}_4\text{N}$. A mixture of 2.5 g of unsaturated monoacetates and 0.2 g of freshly calcined CH_3COONa was heated under water-jet pump vacuum at $125-130^\circ$; after several minutes a mixture of 1-nitropentadiene-1,3 and 1-nitropentadiene-2,4 began to distill off; yield 1 g; b.p. $75-78^\circ$ (8 mm); n_D^{20} 1.5530.

Condensation of Acetaldo1 with Nitroethane. To a mixture of 7.5 g (0.1 M) of nitroethane, 8.8 g (0.1 M) of aldol, and 20 ml of alcohol with cooling (temperature in flask 10°) was added to 10 ml of 10 N NaOH solution (0.1 M) and stirred for 4-5 hours at ~20°. On the following day this was neutralized with dilute H₂SO₄ until weakly acidic,

extracted with ether and the ethereal solution dried with Na_2O_4 . After removal of ether in vacuo the condensation product was obtained as a light-yellow, viscous oil; yield 7.5 g; n_D^{20} 1.4680-1.4700.

Dehydration of Condensation Product of Acetaldo1 with Nitroethane. A mixture of 10 g of oil, n_D^{20} 1.4660, formed by condensing nitroethane with aldol, and 7.5 g of phthalic anhydride was heated under water-jet pump vacuum and a mixture of 1-methyl-1-nitropentadiene-1,3, and 1-methyl-1-nitropentadiene-2,4 distilled off; yield, 5.5 g; n_D^{20} 1.5362; b.p. 93.5° (10 mm); d_4^{20} 1.0623; MR 34.60; Found: MR 35.07; mol. wt. 127; found 130.3 (cryoscopically). Found: C 57.47; 57.42; H 7.17; 7.15; N 11.09; 11.26%. $\text{C}_6\text{H}_9\text{NO}_2$. Calculated: C 57.50; H 7.1; N 11.02%.

Acetylation of Condensation Product of Acetaldo1 with Nitroethane. Into an ethereal solution of 5.5 g of the oil, n_D^{20} 1.4660, obtained by condensing acetaldo1 with nitroethane, with cooling ice water, was bubbled a stream of ketene (10-15% in excess of the amount necessary for acetylating the two diol hydroxyl groups); ether was finally evaporated off in vacuo, the residue distilled and a substance obtained with b.p. 114-114.5° (2 mm); n_D^{20} 1.4381; d_4^{20} 1.1845. Found: C 49.50; 49.96; H 7.02; 7.04%. $\text{C}_8\text{H}_{13}\text{NO}_4$. Calculated: C 50.74; H 7.00%.

Condensation of Acetaldo1 with 2-Nitropropane. To a mixture of 18 g of 2-nitropropane, 30 ml of CH_3OH , and 1.2 g of $\text{Ba}(\text{OH})_2$ was added from a dropping funnel 10 g of aldol, the mixture thereupon warming up a little. After 4 days the clear solution was diluted with water, neutralized with dilute H_2SO_4 , extracted with ether and the ethereal solution dried with Na_2SO_4 . A light-yellow oil was obtained in the residue; yield 14-15 g; n_D^{20} 1.4610-1.4600.

Dehydration of Condensation Product of Acetaldo1 with 2-Nitropropane. A mixture of 13 g of condensation product, n_D^{20} 1.4612, and 20 g of phthalic anhydride was heated under water-jet pump vacuum on a bath at 160-170° and 2-nitro-2-methylhexadiene-3,5 obtained as a mobile, yellow oil, darkening on storage; yield 4.5 g, b.p. 96-98° (10 mm); n_D^{20} 1.5327; d_4^{20} 1.0464. Found: N 10.35; 10.12%. $\text{C}_7\text{H}_{11}\text{NO}_2$. Calculated: N 9.9%.

Condensation of Acetaldo1 with 1,1-Dinitroethane. A mixture of 10 ml of acetaldo1, 15 ml of water, 6 g of 1,1-dinitroethane, and 2 drops of H_2SO_4 was heated for 4 hours at bath temperature 65-70°. On cooling, the product was extracted with ether, the ethereal solution washed with soda, water, dried with Na_2SO_4 and distilled. On distillation of the residue after removal of ether in vacuo, 2,2-dinitro-decanetetrol-3,5,7,9 was obtained; yield 1.5 g; b.p. 74-74.5° (0.008 mm); n_D^{20} 1.4680; d_4^{20} 1.267; MR 65.72; found MR 64.94; mol. wt. 296; found 290.5. Found: C 41.04; 40.94; H 6.02; 5.97; N 9.97; 9.87%. $\text{C}_{10}\text{H}_{20}\text{O}_8\text{N}_2$. Calculated: C 40.54; H 6.76; N 9.46%.

SUMMARY

1. In the case of acetaldo1 and nitromethane, nitroethane, and 2-nitropropane it was shown that in presence of barium hydroxide condensation of acetaldo1 and nitroalkane takes place, the corresponding mononitrodiol being formed, dehydration of which leads to the corresponding mononitrodienes.
2. By condensing acetaldo1 with 1,1-dinitroethane, 2,2-dinitrodecanetetrol-3,5,7,9 is formed.

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AN INVESTIGATION OF THE SYNTHESIS AND TRANSFORMATION OF UNSATURATED SILICON-CONTAINING COMPOUNDS

COMMUNICATION 1: ESTERIFICATION WITH ADIPIC ACID OF PRIMARY AND TERTIARY ACETYLENIC ALCOHOLS WHICH CONTAIN SILICON IN THE GAMMA POSITION

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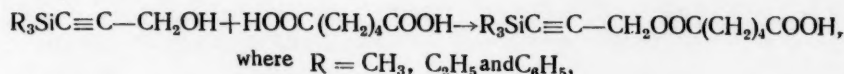
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 4, pp. 699-703, April, 1961

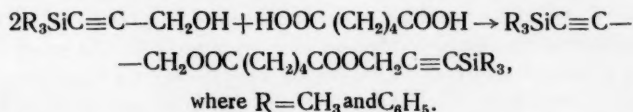
Original article submitted December 15, 1959

The present investigations which we conducted earlier [1-6] on the synthesis and transformation of silicon- and germanium-containing organic acetylenic alcohols have made it possible to obtain much interesting data from the point of view of the reactivity of these compounds, and to obtain from them very interesting derivatives. The reactions investigated included hydrogenation, acetylation, vinylation, dehydration, cyanoethylation, esterification and the exchange of hydroxyl for halogen. A systematic study of the properties of the hetero-organic acetylenic alcohols with the alluring prospect of obtaining from them interesting new substances has compelled us to investigate intensively the esterification of these compounds.

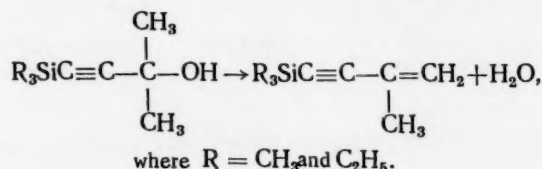
The present investigation is devoted to the study of the esterification with adipic acid of the primary and tertiary acetylenic alcohols which contain silicon in the gamma position. The esterification of these alcohols was carried out by the reaction of the alcohols or of their magnesium derivatives with adipyl chloride. The study of the esterification with adipic acid of the primary acetylenic alcohols which contain silicon in the gamma position in the absence of catalyst showed that depending on the conditions of the synthesis and the ratios of the starting materials, the reaction could proceed to form either the acid esters



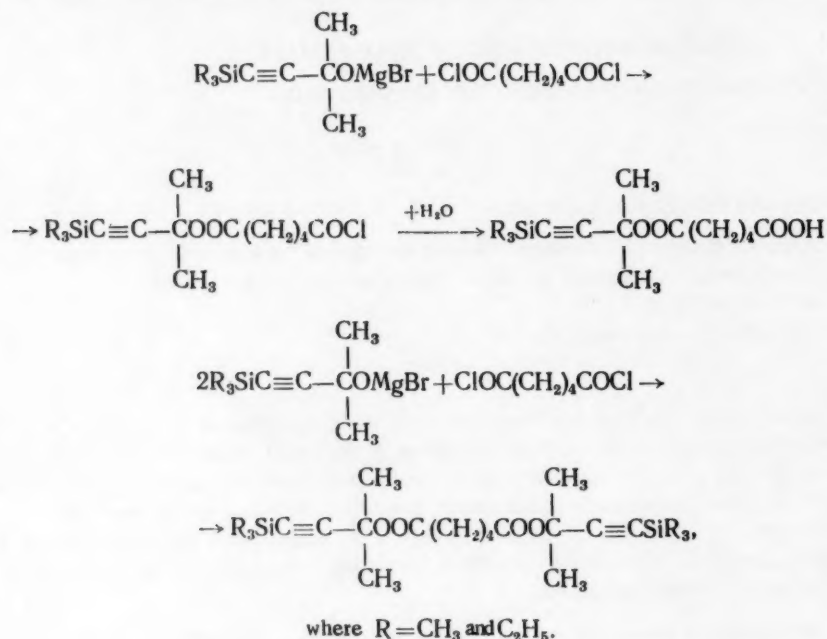
or the full esters of adipic acid



However, this method turned out to be useless for the esterification of the tertiary acetylenic alcohols with adipic acid both in the presence of acid catalysts (p-toluenesulfonic acid, boric acid and others), and in their absence it led to the dehydration of the alcohol to form the corresponding vinylacetylenic silicon-containing hydrocarbon.



An attempt to realize the esterification of the tertiary acetylenic alcohols containing silicon in the gamma position by means of their interaction with adipyl chloride in the presence of pyridine was unsuccessful, as was also an attempt at ester exchange with these alcohols and dimethyl adipate under the influence of sodium ethylate. We succeeded in synthesizing the acid and full esters of the tertiary acetylenic alcohol containing silicon in the gamma position through the interaction of the magnesium alcoholates with adipyl chloride



EXPERIMENTAL PART

1. The following starting materials were used in carrying out the investigations: 4-trimethylsilyl-2-methylbutyne-3-ol-2 [1], b.p. 78° (25 mm) m.p. 42.5° ; 4-triethylsilyl-2-methylbutyne-3-ol-2, b.p. 91° (2 mm); n_D^{20} 1.4462; d_4^{20} 0.8571; 3-trimethylsilylpropyne-2-ol-1 [7], b.p. 61° (2 mm); n_D^{20} 1.4523; d_4^{20} 0.8806; 3-triethylsilylpropyne-2-ol-1 [7], b.p. 109° (6 mm); n_D^{20} 1.4670; d_4^{20} 0.8932; 3-dimethylphenylsilylpropyne-2-ol-1 [7], b.p. 131° (2 mm); n_D^{20} 1.5335; d_4^{20} 0.9996; adipic acid, m.p. 151° ; adipyl chloride, b.p. 116° (7 mm).

The synthesis of mono-3-dimethylphenylsilylpropyne-2 adipate $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SiC}\equiv\text{C}-\text{CH}_2\text{OOC}(\text{CH}_2)_4\text{COOH}$. Adipic acid, 3.65 g (0.025 M) was placed in a three necked 25 ml round bottomed flask furnished with a reflux condenser, a mechanical stirrer, a thermometer, a dropping funnel, and an exit tube. The contents of the flask were heated to the melting point, and to the melted acid was added drop-wise 4.76 g (0.025 M) of 3-dimethylvinylsilylpropyne-2-ol-1. The reaction mixture was stirred and heated for 3 hours at 160° . The water formed in the synthesis was collected via the exit tube in a tared receiver. At the end of the synthesis, the reaction mass was filtered on a glass filter to separate the unreacted adipic acid. The residue was washed several times with dry ether. The filtrate and the residue left from the removal of the dry ether were distilled in vacuo. The substance isolated by distillation weighed 2.0 g (25%), 210° (4 mm); n_D^{20} 1.4960; d_4^{20} 1.067. Found: Si 8.87%; MR 87.18, $\text{C}_{17}\text{H}_{22}\text{SiO}_4$. Calculated: Si 8.85%; MR 88.70.

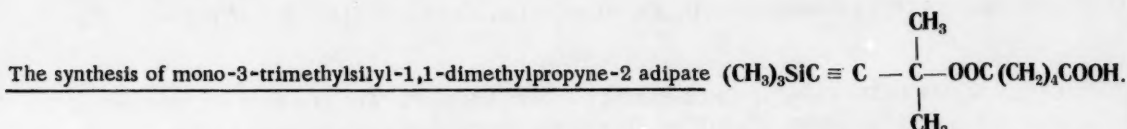
The synthesis of di-(3-dimethylphenylsilylpropyne-2) adipate* $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SiC}\equiv\text{C}-\text{CH}_2\text{OOC}(\text{CH}_2)_4\text{COOCH}_2\text{C}\equiv\text{CSi}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$. In the apparatus described above were placed 9.52 g (0.05 M) of 3-dimethylphenylsilylpropyne-2-ol-1 and 3.65 g (0.025 M) of adipic acid. The mixture was heated to $170-175^\circ$ and stirred for 3 hours. The water formed during the synthesis was collected via the exit tube in a tared receiver. At the end of the synthesis, the

* The mono- and the di-(3-dimethylphenylsilylpropyne-2) adipates were apparently contaminated with disproportionation products.

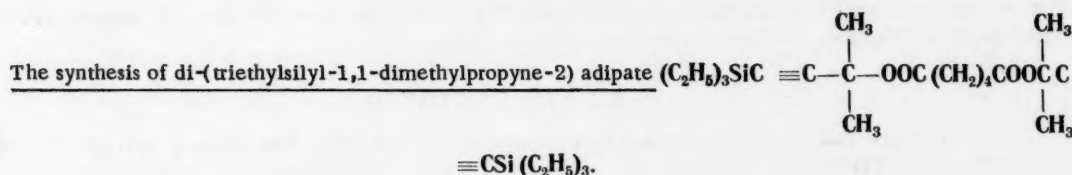
reaction mixture was filtered through a glass filter from the unreacted adipic acid. The precipitate and the filtrate were worked up in a manner analogous to that described above. As a result of the synthesis, 1.23 g (33%) of adipic acid was regained and 4.84 g (39%) of di-(3-dimethylphenylsilylpropyne-2) adipate with b.p. 260° (5 mm); n_D^{20} 1.5112; d_4^{20} 1.0700. Found: Si 10.86%; MR 137.47. $C_{28}H_{34}Si_2O_4$. Calculated: Si 11.44%; MR 144.39.

The synthesis of mono-3-triethylsilylpropyne-2 adipate $(C_2H_5)_3SiC \equiv C-CH_2OOC(CH_2)_4COOH$. The synthesis was carried out in a manner analogous to the synthesis of mono-3-dimethylphenylsilylpropyne-2 adipate. Adipic acid, 3.65 g (0.025 M) and 3-triethylsilylpropyne-2-ol-1, 4.4 g (0.025 M) were used. The yield was 3 g (41%), b.p. 215° (6 mm); n_D^{20} 1.4650; d_4^{20} 1.010. Found: Si 9.39%; MR 81.62. $C_{15}H_{13}SiO_4$. Calculated: Si 9.42%; MR 82.92.

The synthesis of mono-3-triethylsilylpropyne-2 adipate $(CH_3)_3SiC \equiv C-CH_2OOC(CH_2)_4COOH$. The synthesis was carried out as described above. The quantities used were 3.65 g (0.025 M) of adipic acid and 3.2 g (0.025 M) of 3-trimethylsilylpropyne-2-ol-1. The yield was 3.2 g (53%), b.p. 184-185° (4 mm); n_D^{20} 1.4604; d_4^{20} 1.012. Found: Si 11.83%; MR 65.10. $C_{12}H_{10}SiO_4$. Calculated: Si 11.70%; MR 69.03.

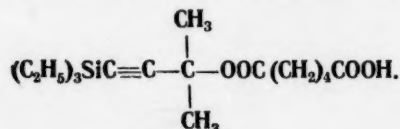


To the Grignard reagent prepared from 2.4 g (0.1 M) of Mg and 10.9 (0.1 M) of ethyl bromide with cooling and stirring, was added drop-wise 15.6 g (0.1 M) of 4-trimethylsilyl-2-methylbutyne-3-ol-2 in 20 ml of absolute ether. The mixture was heated on a water bath for 1 hour. Then 9.2 g (0.05 M) of adipyl chloride was added with cooling and stirring. The reaction mixture was heated on a water bath for 1 hour, and was then treated with a 1 N solution of hydrochloric acid until the residue was completely dissolved. The ether layer was separated from the aqueous layer, and the latter was extracted 3 times with ether. The ether layer and the ether extract were washed with water to free them from HCl, and they were then dried over anhydrous calcium chloride. The ether was removed, and the residue was distilled in vacuo. The yield was 10 g (36%), b.p. 178-180° (4 mm); n_D^{20} 1.4548; d_4^{20} 0.9902. Found: Si 9.88%; MR 77.87; $C_{14}H_{24}SiO_4$. Calculated: Si 9.89%; MR 78.29.



The synthesis was carried out in the manner described above. Mg, 0.84 g (0.035 M) and 3.8 g (0.035 M) of ethyl bromide, were used, followed by 6.9 g (0.35 M) of 4-triethylsilyl-2-methylbutyne-3-ol-2 and 3.2 g (0.0175 M) of adipyl chloride. The yield was 3.1 g (18%), b.p. 198° (2 mm); m.p. 131°. Found: Si 11.47%. $C_{28}H_{50}Si_2O_4$. Calculated: Si 11.09%.

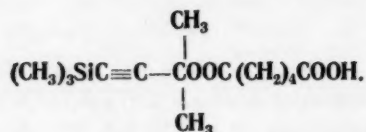
The attempted synthesis of mono-3-triethylsilyl-1,1-dimethylpropyne-2 adipate



The synthesis was carried out analogously to that used for obtaining mono-3-dimethylphenylsilyl-1,1-dimethylpropyne adipate. Adipic acid, 7.3 g (0.05 M), and 4-triethylsilyl-2-methylbutyne-3-ol-2, 10 g (0.05 M) were used. The substances isolated from the synthesis were adipic acid, 7 g and 3 g (32%) of a substance of b.p. 63-65° (14 mm); n_D^{20} 1.4610; d_4^{20} 0.8135. Found: Si 15.52%; MR 60.71. $C_{11}H_{10}Si$. Calculated: Si 15.59%; Mr 60.61. The

analytical data correspond to 4-triethylsilyl-2-methylbutene-1-yne-3 $(\text{C}_2\text{H}_5)_3\text{SiC}\equiv\text{C}-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$ - the product of the dehydration of the alcohol. On standing, the silicon-containing hydrocarbon polymerized to a glass.

The attempted synthesis of mono-3-trimethylsilyl-1,1-dimethylpropyne-2 adipate



The synthesis was carried out in a manner analogous to that given above. Adipic acid, 3.65 g (0.025 M) and 4-trimethylsilyl-2-methylbutyne-3-ol-2, 3.9 g (0.025 M) were used. From the products were isolated 1.77 g of adipic acid and 1.1 g (29%) of substance $(\text{CH}_3)_3\text{SiC}\equiv\text{C}-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$ with b.p. 31° (12 mm); n_D^{20} 1.4445; d_4^{20} 0.7736. Found:

Si 20.30%; MR 46.59. $\text{C}_8\text{H}_{14}\text{Si}$. Calculated: Si 20.31%; MR 46.72. The data from the literature [5] are: b.p. 32-32.5° (15 mm); n_D^{20} 1.4465; d_4^{20} 0.7854. On standing, the product polymerized to a glass.

4-Trimethylsilyl-2-methylbutene-1-yne-3 was obtained also by the interaction of 4-trimethylsilyl-2-methylbutyne-3-ol-2 with adipic acid under the influence of p-toluenesulfonic acid and of boric acid.

SUMMARY

1. The esterification with adipic acid of primary and tertiary acetylenic alcohols which contain silicon in the gamma position was investigated. Methods were worked out for the synthesis of the half and the full adipic esters of the acetylenic alcohols containing silicon in the gamma position.

2. The following compounds were obtained and characterized for the first time: mono-3-dimethylphenylsilylpropyne-2 adipate, di-(3-dimethylphenylsilylpropyne-2) adipate, mono-3-triethylsilylpropyne-2 adipate, mono-3-trimethylsilylpropyne-2-adipate, mono-3-trimethylsilyl-1,1-trimethylpropyne-2 adipate, di-(triethylsilyl-1,1-dimethylpropyne-2) adipate, 4-triethylsilyl-2-methylbutene-1-yne-3.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

AN INVESTIGATION OF THE SYNTHESIS AND TRANSFORMATION OF UNSATURATED SILICON-CONTAINING COMPOUNDS

COMMUNICATION 2: CYANOETHYLATION OF TERTIARY SILICON-CONTAINING ACETYLENIC ALCOHOLS

M. F. Shostakovskii, L. M. Kaliberdo and N. V. Komarov

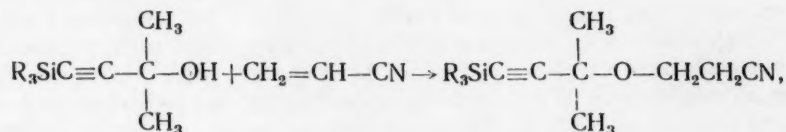
The Institute of Chemistry of the East Siberian Branch of the Siberian Division
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 4, pp. 703-705, April, 1961

Original article submitted December 15, 1959

One of the most general of addition reactions to α,β -unsaturated compounds is the reaction of cyanoethylation. In recent years this reaction has been applied to hetero-organic compounds [1-4]. There are directions in the literature for the cyanoethylation of primary alcohols containing silicon in the α or γ positions [5, 6]. Cyanoethylation of secondary and tertiary silicon-containing alcohols has not been studied, and relative to the interaction of acrylonitrile with the silicon-containing acetylenic alcohols there is no data whatsoever. Nevertheless, there is great interest in the cyanoethylation of organic acetylenic alcohols and glycols.

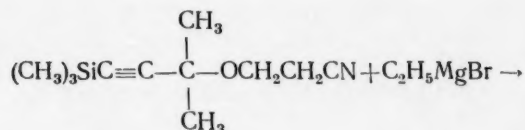
The present investigation is devoted to the study of the cyanoethylation reaction of tertiary acetylenic alcohols containing silicon in the gamma position [7].

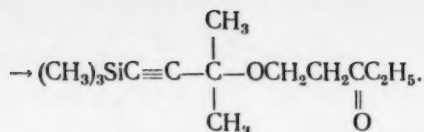


where $\text{R}=\text{CH}_3$ and C_2H_5 .

The cyanoethylation of the tertiary acetylenic alcohols containing silicon in the gamma position was studied under the influence of a 40% aqueous solution of caustic potash and of sodium methylate. The first of these had little catalytic activity — the formation of the corresponding β -cyanoethyl ether was not observed. Nevertheless, corresponding organic analogs are known [8] to form the β -cyanoethyl ethers with yields of 90% under these conditions. The use of sodium methylate as a catalyst led to the synthesis of β -cyanoethyl ethers of the silico-organic acetylenic alcohol with yields of 50-60%. The reaction mixture became warm. Higher yields of the desired products were obtained when the reaction was carried out in a benzene medium rather than in the absence of a solvent.

The interaction of the β -cyanoethyl ether of 4-trimethylsilyl-2-methylbutyne-3-ol-2 with ethyl magnesium bromide was investigated as an example of the reaction of the β -cyanoethyl ethers with the Grignard reagent. As a result of a series of syntheses, it was established that the reaction proceeds with the formation of the corresponding silico-organic acetylenic ketones according to the scheme





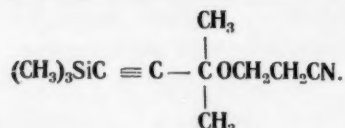
The presence of a carbonyl group in the product compound was proven by the formation of a 2,4-dinitrophenylhydrazone.

However, together with the formation of the silico-organic ketone according to the scheme given above, there also occurs a decomposition of the β -cyanoethyl ether with the formation of 4-trimethylsilyl-2-methylbutyne-3-ol-2. Other transformations of the β -cyanoethyl ethers of tertiary acetylenic alcohols containing silicon in the gamma position will be described in subsequent communications.

EXPERIMENTAL PART

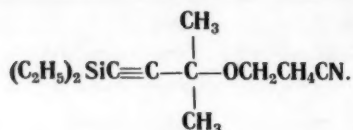
The following starting materials were used for the synthesis of the β -cyanoethyl ethers of the tertiary acetylenic alcohols containing silicon in the gamma position: 4-trimethylsilyl-2-methylbutyne-3-ol-2 [8], b.p. 78° (25 mm); m.p. 42.5°; 4-triethylsilyl-2-methylbutyne-3-ol-2, b.p. 91° (2 mm); n_D^{20} 1.4462; d_4^{20} 0.8574; acrylonitrile, b.p. 78° (731 mm); n_D^{20} 1.3911; d_4^{20} 0.8072.

The synthesis of the β -cyanoethyl ether of 4-trimethylsilyl-2-methylbutyne-3-ol-2



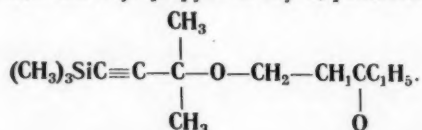
In a 3-necked, 200 ml, round bottomed flask furnished with a reflux condenser, mechanical stirrer, dropping funnel and thermometer were placed 15.6 g (0.1 M) of 4-trimethylsilyl-2-methylbutyne-3-ol-2 and 15 ml of benzene. Sodium methylate, 1.5 ml was introduced, and then 10.6 g (0.2 M) of acrylonitrile was added dropwise with stirring. At 10 min intervals during this time, 1 ml aliquots of sodium methylate were added to the reaction mixture. The mixture became warm. The temperature of the reaction mass rose to 52°. After the addition of the acrylonitrile, the mixture was stirred for an additional 4 hours. The reaction mixture was then neutralized with dilute hydrochloric acid (1:1), and was filtered on a glass filter. The benzene was distilled from the filtrate, and the residue was distilled in vacuo. After two distillations, 12.55 g of a product was obtained with b.p. 120° (14 mm); 123.5-123.7° (16 mm); n_D^{20} 1.4452; d_4^{20} 0.8879; yield 60%. Found: Si 13.73%; MR 62.65; $\text{C}_{11}\text{H}_{19}\text{SiON}$. Calculated: Si 13.44%; MR 62.73.

The synthesis of the β -cyanoethyl ether of 4-triethylsilyl-2-methylbutyne-3-ol-2



The synthesis was carried out in a manner analogous to the preceding. Acrylonitrile (15.9 g) (0.3 M) and 4-triethylsilyl-2-methylbutyne-3-ol-2, 19.8 g (0.1 M) were used, together with 15 ml of benzene and 5 ml of sodium methylate. The yield was 12.52 g (50%), b.p. 136° (2 mm); 140-140.5° (4 mm); n_D^{20} 1.4513; d_4^{20} 0.8925. Found: Si 11.87%; MR 75.79. $\text{C}_{14}\text{H}_{25}\text{SiON}$. Calculated: Si 11.15%; MR 76.62.

The synthesis of (3-trimethylsilyl-1,1-dimethylpropyne-2-oxy-1) pentanone-3



The β -cyanoethyl ether of 4-trimethylsilyl-2-methylbutyne-3-ol-2, 6 g (0.0235 M) was added drop-wise at room temperature and with energetic stirring to the Grignard reagent prepared from 1.4 g (0.06 M) of magnesium and 6.48 g (0.06 M) of ethyl bromide. The reaction mixture was then stirred for 3 hours, and was treated with dilute hydrochloric acid (1: 20) until the precipitate was transformed into a lumpy mass. The ether layer was separated from the solid on a Buchner funnel, the solid was washed with ether, the filtrates were dried over anhydrous potash, the ether was distilled off, and the residue was distilled in vacuo. There were isolated 1.44 g (41%) of 4-trimethylsilyl-2-methylbutyne-3-ol-2 and 1.41 g (22.1%) of (3-trimethylsilyl-1,1-dimethylpropyne-2-oxy-1) pentanone-3 with b.p. 133-134° (25 mm); n_D^{20} 1.4440; d_4^{20} 0.8798. Found: Si 12.62%; MR 72.34. $C_{13}H_{24}SiO_2$. Calculated %: Si 11.70%; MR 72.11. The 2,4-dinitrophenylhydrazone $C_{18}H_{28}SiO_5N_4$ was crystallized from alcohol, m.p. 74°.

SUMMARY

1. The cyanoethylation of tertiary acetylenic alcohols containing silicon in the gamma position was studied.
2. The interaction of magnesium organic compounds with the β -cyanoethyl ethers of the tertiary acetylenic alcohols containing silicon in the gamma position was investigated.

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CHEMICAL TRANSFORMATIONS OF UNSATURATED AND
AND HIGH-MOLECULAR COMPOUNDS

18. POLYMERIZATION AND COPOLYMERIZATION OF DIVINYL TARTRATE
AND METHYL METHACRYLATE

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The polymerization and copolymerization of diallyl esters of dibasic acids have been described [1, 2], and some details have been published of the polymerization and copolymerization of divinyl esters of dibasic hydroxyacids [3, 4]. Nothing has been published about the polymerization and copolymerization of divinyl esters of dibasic hydroxyacids although high-molecular products from these compounds can have considerable theoretical and practical interest. In the present communication we describe the polymerization of divinyl tartrate, which we synthesized earlier [5], and its copolymerization with methyl methacrylate.

Polymerization of divinyl tartrate was carried out in presence of azodiisobutyronitrile and benzoyl peroxide. In order to clarify the influence of the hydroxyl groups in divinyl tartrate on its susceptibility to polymerization, we performed experiments on the polymerization of divinyl adipate which does not contain hydroxyl groups. Results are set forth in Table 1.

We see from Table 1 that yields of polymers of divinyl tartrate are very much lower than those of the polymer of divinyl adipate. The hydroxyls in divinyl tartrate evidently diminish its polymerizability.

TABLE 1. Polymerization of Divinyl Tartrate and Divinyl Adipate

Monomer	Initiator	Quantity of initiator in % of wt. of monomer	Reaction temperature, (°C)	Duration of reaction (hr)	Yields of polymers wt.-%	Properties of polymer
Divinyl tartrate	Azodiisobutyronitrile	0.2	60	100	9	Linear polymer
Ditto	Benzoyl peroxide	0.2	60	100	26	Cross-linked polymer
Divinyl adipate	Azodiisobutyronitrile	0.2	60	3	90	Cross-linked polymer

Copolymerization of divinyl tartrate with methyl methacrylate was studied with various molar ratios of monomers in presence of azodiisobutyronitrile and benzoyl peroxide. The relation between composition and yield of copolymers and initial molar ratio is plotted in Fig. 1.

We see from Fig. 1 that the chemical structure of the initiators influences the yield and composition of the copolymers. Divinyl tartrate - methyl methacrylate copolymerization in presence of benzoyl peroxide gives a higher copolymer yield and a higher content of divinyl tartrate units in the copolymer than copolymerization in presence of azodiisobutyronitrile. Composition and yields of copolymers also depend on the initial monomer ratio. With increasing content of divinyl tartrate in the initial mixture, the copolymer yields decrease and the number of divinyl tartrate units in the copolymer increases. The maximum content of divinyl tartrate units in the copolymer is about

TABLE 2. Yields and Compositions of Copolymers of Methyl Methacrylate (MMA) with Divinyl Tartrate (DVT) (initiator azodiisobutyronitrile)

Ratio of initial monomers, mole-%		Content of initial monomers, g		Polymer yields, %	Empirical analyses, %		Molar composition of copolymer units, %		Quantity of unreacted DVT, g
MMA	DVT	MMA	DVT		C	H	MMA	DVT	
100	—	5	—	97,9	59,82	8,14	100	—	—
90	10	4,08	0,92	63,8	59,74	8,13	100	—	0,8
					61,16	7,90			
					61,25	7,98			
75	25	2,99	2,01	56,0	59,14	7,83	96,2	3,8	1,76
					58,99	7,77			
50	50	1,66	3,34	35,8	58,51	7,41	93,96	6,04	2,81
					58,61	7,46			
25	75	0,71	4,29	17,4	55,50	6,76	77,7	22,3	3,69
					55,32	6,62			
10	91	0,26	4,74	10,6	52,60	5,89	57,2	42,8	3,76
					52,38	5,82			
—	100	—	5	9,1	48,61	5,03	—	100	4,4
					48,56	5,04			

TABLE 3. Yields and Compositions of Copolymers of Methyl Methacrylate (MMA) with Divinyl Tartrate (DVT) (initiator benzoyl peroxide)

Ratio of initial monomers, mole-%		Content of initial monomers, g		Polymer yields, %	Empirical analyses, %		Molar composition of copolymer units, %		Quantity of unreacted DVT, g
MMA	DVT	MMA	DVT		C	H	MMA	DVT	
100	—	5	—	98,6	59,98	8,16	100	—	—
					59,96	8,21			
90	10	4,08	0,92	64,8	60,61	7,92	100	—	0,68
75	25	2,99	2,01	63,0	60,70	8,06	96,4	3,6	1,37
					59,22	7,69			
					59,03	7,62			
50	50	1,66	3,34	50,0	56,75	7,18	85,7	14,3	2,04
					56,98	7,10			
25	75	0,71	4,29	39,2	52,99	6,05	61,1	38,9	2,42
					52,95	6,04			
10	90	0,26	4,74	36,6	51,40	5,62	46,6	53,4	2,53
					51,15	5,52			
—	100	—	5	27,2	49,66	4,97	—	100	2,80
					49,53	4,97			

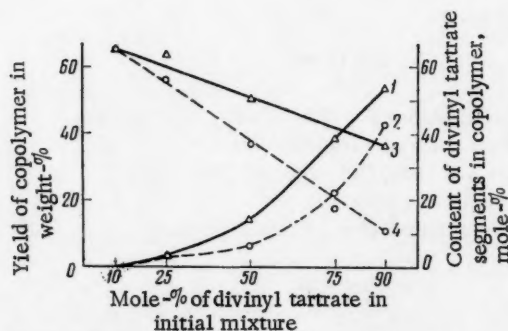


Fig. 1. Relation between yield and composition of copolymers of divinyl tartrate and methyl methacrylate and ratio of initial monomers: Δ) benzoyl peroxide as initiator; \circ) azodiisobutyronitrile as initiator; 1 and 2) content of divinyl tartrate segments in copolymer; 3 and 4) yields of copolymers.

50%. This interesting characteristic, similar to that observed in the copolymerization of vinyl ethers [6], evidently reflects the influence of the two hydroxyls in the molecule. The copolymers are insoluble in organic solvents and infusible, i.e., they have a cross-linked structure.

Experiments were run with low degrees of conversion of the initial monomers with the objective of calculating the relative activities of radicals of methyl methacrylate (r_1) and divinyl tartrate (r_2) in the copolymerization reaction. Constants were calculated with the help of the integral equation and the graphical method of [7]. The relative activity constants are $r_1 = 0.97 \pm 0.02$ (methyl methacrylate) and $r = 0.04 \pm 0.01$ (divinyl tartrate).

EXPERIMENTAL

Freshly distilled monomers were used and they had the following constants: Divinyl tartrate, b.p. 125-126° (2 mm), n_D^{20} 1.4516; methyl methacrylate, b.p. 35-36° (65 mm), n_D^{20} 1.4150; divinyl adipate [3], b.p. 98-98.5° (3 mm), n_D^{20} 1.4548.

Copolymerization was carried out in glass ampoules at $60 \pm 0.5^\circ$ for 100 hr. Reaction initiators were azodiisobutyronitrile and benzoyl peroxide in the proportion of 0.2% of the total weight of monomers. The latter were taken in various molar ratios and their total weight in the ampoule was 5 g. Control runs with individual monomers were carried out under the same conditions. The ampoules were cooled to 0° after completion of the reaction. Solubilities were then determined. The cross-linked polymers were extracted with benzene until the extract gave a negative reaction for the double bond; they were then dried in vacuo to constant weight, and analyzed for carbon and hydrogen. The molar make-up of the copolymer units was calculated from the results of analysis of the divinyl tartrate - methyl methacrylate copolymers. The benzene extract was evaporated in vacuo for determination of the unreacted divinyl tartrate.

Polymerization of initial monomers. Control runs in presence of azodiisobutyronitrile and benzoyl peroxide were carried out in order to determine the susceptibility of the monomers to free-radical polymerization. Heating of divinyl tartrate with azodiisobutyronitrile at 60° for 100 hr gave a polymer soluble in acetone and benzene. The benzene solution of the polymer decolorized bromine water. Yield of polymer 9.09%. Polymerization of divinyl tartrate in presence of benzoyl peroxide at 60° for 100 hr gave a polymer insoluble in acetone and benzene. Polymer yield 27.17%. Heating of divinyl adipate at 60° for 3 hr in presence of azodiisobutyronitrile gave a solid polymer, insoluble in organic solvents; polymer yield 90.24%.

Divinyl tartrate - methyl methacrylate copolymerization. The above procedure was followed. Results are set forth in Tables 2 and 3. It should be noted that results of empirical analysis of divinyl tartrate polymers deviate from the theoretical values by 1-2%, evidently due to internal changes in the divinyl tartrate molecule.

SUMMARY

1. Polymers of divinyl tartrate were synthesized with both linear and cross-linked structures. It is suggested that the hydroxyl groups in divinyl tartrate lower its susceptibility to polymerization in comparison with vinyl esters not containing a hydroxyl group.

2. The copolymerization of divinyl tartrate with methyl methacrylate was studied. Cross-linked copolymers were obtained.

3. Constants of relative activity of radicals in copolymerization of methyl methacrylate with divinyl tartrate were calculated.

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THE DIENE SYNTHESIS WITH PARTICIPATION OF VINYL ETHERS

5. REACTION OF DIVINYL ETHER WITH HEXACHLOROCYCLOPENTADIENE

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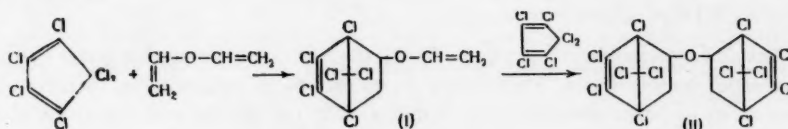
Translated from *Izvestiya Akademii Nauk, Otdelenie Khimicheskikh Nauk*,

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Divinyl ether occupies a special position in the vinyl ether class because it contains two vinyl groups which enable the preparation of two series of derivatives. We previously [1] studied the reaction of divinyl ether with carbon tetrachloride under the influence of various reagents and factors that initiated the reaction by a radical mechanism. A series of new α -chloroethers was isolated which contained chlorinated saturated and unsaturated radicals. In a systematic study [2] of the diene synthesis with participation of vinyl ethers, we considered using divinyl ether in the reaction, especially since very little has been published in this field. A patent [3] mentions the isolation of one adduct and the possibility of its polymerization in presence of boron trifluoride etherate.

In the present work we studied the conditions of interaction of divinyl ether with hexachlorocyclopentadiene and some properties of the resulting adducts. Stepwise reaction takes place due to the presence of two vinyl groups in the ether, and it leads to formation of adducts (I) and (II) whose yields depend on the ratio of the initial components and on the reaction temperature.



Adduct (I) is vinyl 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-ol ether. It has some of the properties of these ethers but also some special characteristics. It differs from previously studied vinyl ethers [4-6] in being more difficult to hydrolyze. Prolonged heating with 2% sulfuric acid gave a good yield of crystalline 1,4,5,6,7,7-hexachlorobicyclo 2,2,1 -hept-5-en-2-ol (III) (equation 2).

Polymerization of the vinyl ether in presence of boron trifluoride etherate only goes when heat is applied. A solid polymer was obtained in good yield. Addition of carbon tetrachloride under the usual conditions could not be effected, in presence of azodiisobutyronitrile; the product was a polyvinylhexachlorobicycloheptenyl ether. It was particularly interesting to find that the resulting vinyl ether was susceptible to polymerization by a radical mechanism under the influence of azodiisobutyronitrile. The polymer did not melt at 300°. Polymers obtained under the influence of boron trifluoride etherate and of azodiisobutyronitrile differ in physical properties (solubility, softening point, molecular weight). Reaction of vinyl hexachlorobicycloheptenyl ether with hydrogen chloride goes under the same conditions as for vinyl alkyl and vinyl aryl ethers [7]. The resulting α -chloroethyl 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl ether (IV) is stable in storage, and it cannot be titrated with 0.1 NaOH without previous hydrolysis which takes place slowly at room temperature [8]. (equation 3). Interaction of the α -chlorine with ethylmagnesium bromide leads to 2-sec. butoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-heptene-5 (V) (equation 4).

band caused by other structural elements common to (I) and (II). Due to the influence of the bicycloheptene ring the valence vibration frequency of the ether group in adduct (II) is somewhat low; the absorption band is at 1107 cm^{-1} (the absorption bands of the ether group are in the $1150\text{--}1160\text{ cm}^{-1}$ region) [11]. Only one double-bond absorption band was found in the spectrum of the polymer of vinyl hexachlorobicycloheptenyl ether (at 1609 cm^{-1}), and we may therefore say that polymerization occurred at the expense of the vinyl group.

EXPERIMENTAL

Reaction of divinyl ether with hexachlorocyclopentadiene (Eq. 1). a) In 2:1 ratio. A sealed ampoule containing 30.0 g (0.43 M) of divinyl ether and 48.9 g (0.18 M) of diene was heated on a boiling water bath for 4 hr. The content of the ampoule was then transferred to a flask and fractionated. The fraction (13.2 g) with b.p. $24\text{--}32^\circ$ at atmospheric pressure contained divinyl ether with a trace of acetaldehyde. Fractionation in vacuo gave a fraction with b.p. $118.5\text{--}119.5^\circ$ (3 mm) (42.1 g) which was 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl vinyl ether (I); n_D^{20} 1.5460; d_4^{20} 1.5622; found MR 69.50. $\text{C}_9\text{H}_6\text{Cl}_6\text{O} \cdot 2\text{E}$. Calculated MR 69.47. Found C 31.62, 31.69; H 1.77, 1.87; Cl 61.79, 62.01%. Calculated C 31.53; H 1.77; Cl 62.05%. Yield 51.2% of the theoretical calculated on the ether reacted. Literature data [3]: b.p. 79° (0.8 mm); n_D^{21} 1.5478.

The dark-red, glassy residue was treated with methanol in the cold and gave 11.2 g (13.4% of theory) of crystalline bis-(1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl) ether (II) with b.p. $141\text{--}142^\circ$ (from heptane); b.p. $140\text{--}143.5^\circ$ (7×10^{-3} mm). Found: C 27.50, 27.53; H 0.95, 0.95; Cl 69.00, 68.79%. $\text{C}_{14}\text{H}_6\text{Cl}_{12}\text{O}$. Calculated: C 27.30; H 0.98; Cl 69.10%.

b) In 1:1 ratio. From 10.8 g (0.04 M) of diene and 2.8 g (0.04 M) of ether, heated in an ampoule for 6 hr at $100\text{--}115^\circ$, were obtained 5.5 g (40.5% of theory) of vinyl hexachlorobicycloheptenyl ether (I) and 4.95 g (22% of theory) of bis-hexachlorobicycloheptenyl ether (II).

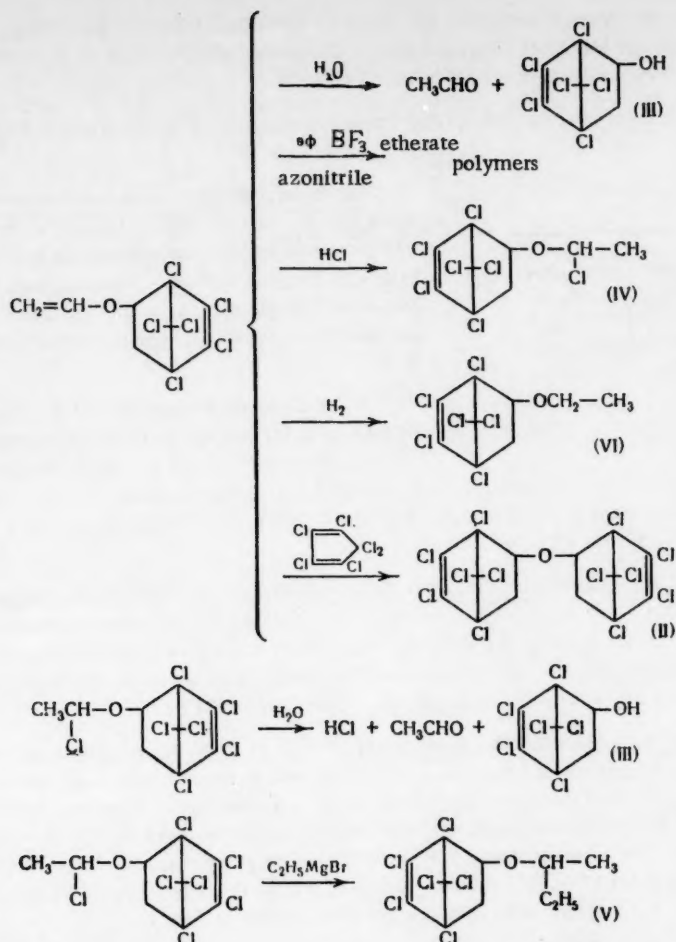
Condensation of vinyl hexachlorobicycloheptenyl ether (I) with hexachlorocyclopentadiene (Eq. 2). A mixture of 3.4 g (0.01 M) of vinyl ether and 2.7 g (0.01 M) of diene was heated for 10 hr at $100\text{--}110^\circ$ in a sealed ampoule. The mass in the ampoule crystallized on cooling. There was obtained 5.4 g (88% of theory) of bis-hexachlorobicycloheptenyl ether (II) with m.p. $141\text{--}142^\circ$ (from n-heptane).

Hydrogenation of hexachlorobicycloheptenyl vinyl ether (I) (Eq. 2). A hydrogenation vessel was charged with 5.3 g of vinyl ether in 15 ml of dry n-heptane. Hydrogenation was carried out over platinum oxide prepared by the Adams method. The amount of hydrogen absorbed after 15 min was 320 ml (the theoretically required volume is 346 ml). After the solvent had been removed, the reaction mixture was fractionated in vacuo to give 4.5 g (84.4% of theory) of 2-ethoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-heptene-5 (VI) with b.p. $125\text{--}126^\circ$ (3.5 mm); n_D^{20} 1.5342; d_4^{20} 1.5322; found MR 70.00; $\text{C}_9\text{H}_6\text{Cl}_6\text{OE}$. Calculated MR 69.74. Literature data [12]: b.p. $134\text{--}135^\circ$ (5 mm); d_4^{20} 1.5576; n_D^{20} 1.5358. Found: C 31.34, 31.27; H 2.38, 2.36; Cl 61.73, 61.86%. Calculated: C 31.37; H 2.34; Cl 61.73%.

Addition of HCl to vinyl hexachlorobicycloheptenyl ether (I) (Eq. 2). A mixture of 4.2 g of vinyl ether and 10 ml of dry diethyl ether was placed in a three-necked flask equipped with stirrer, thermometer, and reflux condenser. A stream of dry HCl was passed in with cooling to -5 to -7° . The reaction mixture became saturated in the course of an hour. After removal of the solvent, the reaction product was distilled in a dry nitrogen stream. There was obtained 4.6 g of product with a pleasant odor which was identified as α -chloroethyl 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl ether (IV) with b.p. $91.3\text{--}91.5^\circ$ (9×10^{-3} mm); n_D^{20} 1.5403; d_4^{20} 1.5682; Found MR 75.97. $\text{C}_9\text{H}_7\text{Cl}_7\text{O}$. Calculated MP 74.61. Found: C 28.82, 29.09; H 1.91, 2.00; Cl 66.22, 65.04%. Calculated: C 28.49; H 1.85; Cl 65.43%. Yield 99% of the theoretical.

a) Hydrolysis of α -chloroethyl hexachlorobicycloheptenyl ether and determination of the acid equivalent (eq. 3). A weighed sample of the ether was put into a flask (with a ground-glass stopper) containing 25 ml of distilled water. After mechanical stirring for 2 hr, the HCl was determined by titration with 0.1 N NaOH solution [7]. 0.5501 g of substance consumed 13.35 ml of 0.1 N NaOH; 0.3265 g of substance consumed 7.85 ml of 0.1 N NaOH. Acid equivalent found: 431.0; 435.1; $\text{C}_9\text{H}_7\text{Cl}_7\text{O}$. Calculated 279.4.

b) Reaction of α -chloroethyl hexachlorobicycloheptenyl ether with $\text{C}_2\text{H}_5\text{MgBr}$. The α -chloroether (5.2 g) in diethyl ether was slowly added to an equimolar quantity of ethylmagnesium bromide prepared from 0.33 g of Mg and 1.5 g of $\text{C}_2\text{H}_5\text{Br}$. Heat was liberated. The mixture was allowed to stand overnight and then decomposed with 10%



Hydrogenation [4] of vinyl hexachlorobicycloheptenyl ether over platinum oxide at room temperature gave 2-ethoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-heptene-5 (VI). The vinyl group of this ether easily undergoes diene synthesis with hexachlorocyclopentadiene with formation in good yield of bis-(1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl) ether (II) which has low chemical activity.

The foregoing transformations of 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-yl vinyl ether are shown in Eq. (2). The relative inertness in ionic and radical reactions of the vinyl group in the molecule of vinyl hexachlorobicycloheptenyl ether may be attributed to the influence of the hexachlorobicycloheptenyl radical which weakens its oxonium properties and consequently hinders formation of activated molecules. The result is that the properties of the vinyl group of the ether approximate to those of an ordinary double bond.

The infrared spectra of adducts from diene synthesis of divinyl ether with hexachlorocyclopentadiene (I) and (II) were plotted for more complete characterization.* The spectra of the hexachlorobicycloheptenyl vinyl and bishexachlorobicycloheptenyl ethers have characteristic strong bands at 1603 and 1613 cm^{-1} respectively which must be assigned to the vibrations of the double bond of the bicycloheptene ring [9, 2]. The presence of a vinyl group in adduct (I) is confirmed by the two strong absorption bands at 1626 and 1641 cm^{-1} . Adduct (I) would be expected to contain an absorption band in the 1020-1057 cm^{-1} region [10] characteristic of the ether group of a vinyl ether. There are two strong bands at 1066 and 1037 cm^{-1} . Comparison of the spectra of (I) and (II) showed that the ether group of adduct (I) is associated with the 1037 cm^{-1} band since the spectrum of adduct (II) also contains a strong 1065 cm^{-1}

* The spectra were plotted by B. V. Lopatin, a co-worker of the optical laboratory of the Institute of Organic Chemistry, AN SSSR.

HCl. The upper layer was washed and dried over calcium chloride. Yield 3.7 g with b.p. 129.5-130.5° (2 mm); n_D^{20} 1.5235; d_4^{20} 1.4362; Found MR 79.41. $C_{11}H_{12}Cl_6O$. Calculated MR 78.98. Found: C 35.69; 35.90; H 3.22; 3.30; Cl 57.01; 56.87%. Calculated: C 35.42; H 3.24; Cl 57.05%.

The product was 2-sec. butoxy-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-heptene-5 (V). Yield 51.2% of the theoretical.

Weight of ether, g	Duration of hydrogenation, hr	Degree of hydrolysis, %
0,2087	9	64,07
0,2257	10	72,13
0,2427	11	77,00

Hydrolysis of vinyl hexachlorobicycloheptenyl ether (I) with 2% H_2SO_4 (Eq. 2). a) A weighed sample of the substance and 20 ml of 2% H_2SO_4 were sealed into an ampoule and heated on a boiling water bath with frequent shaking. After cooling, the ampoule was opened. The acetaldehyde content of the hydrolysis product was determined by the bisulfite method [5]. Results of hydrolysis are set forth in the table.

b) A flask was charged with 3 g of vinyl ether and 100 ml of 2% sulfuric acid, and the mixture was heated with vigorous stirring on a boiling water bath for 17 hr. A crystalline product was obtained in the amount of 2.4 g (86% of the theoretical); m.p. 152-153.5° (from n-heptane). It was identified as 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-en-2-ol (III). Found: C 26.91, 26.95; H 1.36; 1.44; Cl 66.97; 67.08%; $C_7H_4Cl_6O$. Calculated C 26.54; H 1.27; Cl 67.14%.

Reaction of vinyl hexachlorobicycloheptenyl ether with CCl_4 . An ampoule was charged with 2.5 g of the ether, 3.5 g of CCl_4 (molar ratio 1: 3), and 0.07 g of azodiisobutyronitrile. The mixture was heated to 170-175° for 4 hr. After distillation of the excess of CCl_4 , the dark, viscous product was reprecipitated from ethereal solution by methanol. The light colored powder was a polymer of the initial vinyl hexachlorobicycloheptenyl ether; it did not melt at 230°. Found: Cl 61.36, 61.46%. $(C_9H_6OCl_6)_n$. Calculated: Cl 62.05%.

Polymerization of vinyl hexachlorobicycloheptenyl ether. a) With BF_3 etherate. A flask was charged with 1.63 g of the ether, and three drops of 5% solution of BF_3 etherate in diethyl ether were added. The flask was then heated for 30 min at 75-80°, and thereafter for 4 hr at 50-60°. A transparent, colorless, very viscous product was obtained. The polymer was twice reprecipitated from solution in diethyl ether by dry methanol and dried at 60° (3 mm) to constant weight. There was obtained 1.37 g (96.6%) of polyvinyl hexachlorobicycloheptenyl ether as a white powder. Softening point 175-185°. Found: C 32.11, 32.26; H 1.92; 1.91; Cl 61.48; 61.21%. $(C_9H_6Cl_6O)$. Calculated: C 31.53; H 1.77; Cl 62.05%; mol. weight 2693; 2720; η 0.6811.

The polymer is soluble in diethyl ether, acetone, benzene, toluene, chloroform, and CCl_4 ; insoluble in methanol, ligroine, and gasoline.

b) With azodiisobutyronitrile. Into an ampoule were sealed 4.6 g of the ether and 0.24 g of the nitrile. Heating was effected in a thermostat at 60° for 100 hr. The content of the ampoule was dissolved in benzene and reprecipitated by methanol. There was obtained 1.6 g (33%) of white powder which did not melt at 300° and decomposed at higher temperatures. The polymer is soluble in benzene, toluene, chloroform, and CCl_4 ; insoluble in diethyl ether, n-heptane, ligroine, methanol, and gasoline. Found: molecular weight 1096, 1073.

SUMMARY

1. Reaction of divinyl ether with hexachlorocyclopentadiene gives, depending on the experimental conditions, varying yields of mono- and diadducts. Their properties are studied.

2. Attention is drawn to some differences between the characteristics of the resulting vinyl hexachlorobicycloheptenyl ether (monoadduct) and those of previously known vinyl ethers. These differences arise from the nature of the hexachlorobicycloheptenyl radical.

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ALKYLATION OF NORMAL PARAFFINS WITH OLEFINS AT HIGH TEMPERATURES AND PRESSURES

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Interaction of saturated hydrocarbons with unsaturated hydrocarbons is a complex process in which two main reactions compete: alkylation of the paraffin and polymerization of the olefin.

In preceding investigations we established that realization of the process of alkylation in presence of alumina calls for high temperature (450-500°) and high pressure (400-500 atm). In the present work we carried out experiments under the same conditions in presence of tricalcium phosphate. Comparison of the results with those obtained in presence of quartz showed that interaction of components with a short carbon chain (propane - ethylene) proceeds thermally, while that of hydrocarbons with a longer chain (butane - propylene) proceeds thermocatalytically. The results permitted in a number of conclusions about the mechanism of the alkylation process. A characteristic feature of the process is formation of hydrocarbons whose structure is governed by interaction of the most reactive carbon atom of the paraffin with the olefin molecule without isomerization of the skeleton. This picture differs from that in low-temperature alkylation in presence of acid catalysts when products of isomerization of the expected hydrocarbons are obtained.

EXPERIMENTAL

Experiments were carried out under dynamic conditions in the apparatus described earlier [1]. Mixture of gaseous and liquid hydrocarbons (n-hexane, isopentane) were pressed into the reactor with the help of a liquid pump. Space velocities for gas mixtures (C_2-C_4) are expressed as liters of gas per liter of catalyst per hour; for gas - liquid mixtures they are expressed as liters of liquid per liter of catalyst per hour. The yield of alkylate is calculated in weight-% of the olefin taken into reaction; the yield of individual fractions is referred to the total alkylate.

We used a commercial calcium phosphate and also one prepared by us (phosphate P); experiments with the latter are indicated by an asterisk in the tables. Phosphate P was prepared by precipitation from highly dilute solutions of diammonium phosphate and calcium chloride in presence of ammonia. Technical hydrocarbons were used in the work. The n-butane had 97% purity. The propane contained 7.8% of ethane and 1.4% of n-butane; the propylene contained 14% of propane, and the ethylene 6.1% of ethane. The n-hexane had b.p. 69.7°, d_4^{20} 0.6594, n_D^{20} 1.3753. The isopentane had b.p. 27.0°, d_4^{20} 0.6213, n_D^{20} 1.3565. The butylene contained 7% of n-butane and 2.5% of ethylene.

Alkylates were fractionated in a 70-plate column. Interest was attached mainly to products of interaction of a molecule of paraffin with one or two molecules of olefin. Narrow cuts were chromatographed on silica gel with the objective of elimination of unsaturated hydrocarbons from them; their bromine number and refractive index were determined. The saturated hydrocarbons obtained were characterized by their constants and identified by their Raman spectra.

Alkylation of propane and n-butane by ethylene. Conditions and results of experiments are detailed in Tables 1 and 2. We see from Table 1 that the highest yields of alkylate and of the expected pentane fraction are obtained at 500° and 450 atm. In presence of crushed quartz the yield is greater than that obtained with calcium phosphate. Ethylene was converted to the extent of 75%.

The fractionation curve of the alkylate of expt. 6 (Table 1) is plotted in Fig. 1. The three horizontal portions (1, 2, and 3) on this curve correspond to two narrow pentane cuts and an isoheptane cut. After removal of unsaturated impurities, hydrocarbons with the following constants were obtained: I) b.p. 26-27°, d_4^{20} 0.6206, n_D^{20} 1.3550; II)

TABLE 1

Experimental conditions and composition of alkylate	Catalyst				
	phosphate		quartz		
	experiment number				
	1	3	5*	6	7
Temperature, °C	450	500	500	450	500
Pressure, atm	450	300	450	450	450
Propane: ethylene (volumetric)	3,5	5,5	4,6	6,0	7,0
Space velocity	1800	3000	2300	1800	1100
Degree of ethylene conversion, %	55	42	75	64	72
Yield of alkylate, weight-%	60	53	122	102	109
Yield of fractions, weight-%					
25-30°	6,9		27,3	23,2	31,8
30-38°	4,5		8,5	10,2	13,2
38-85°	11,0	15,0	12,6	11,2	21,6
85-95°	11,1	16,7	12,0	12,3	10,5
High-boiling residue	69,5	60,0	39,6	43,0	30,7

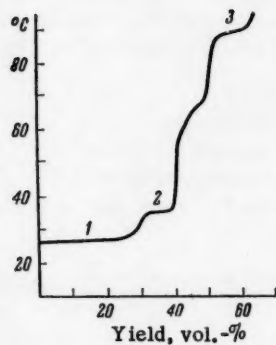


Fig. 1.

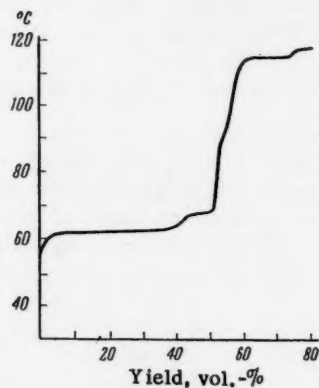


Fig. 2.

TABLE 2

Experimental conditions and composition of alkylate	Catalyst				
	phosphate		quartz		
	experiment number				
	8	9	12*	13	14
Temperature, °C	450	450	500	450	450
Pressure, atm	300	450	450	450	450
Butane: ethylene (by volume)	5	5	4,5	3	5
Space velocity	2400	650	1500	1200	1100
Degree of conversion of ethylene	25	36	70	60	56
Yield of alkylate, weight-%	60	185	126	82	110
Yield of fractions, weight-%					
up to 60°	27,0	1,4	4,4	2,6	1,3
60-65°	13,8	36,4	28,6	16,3	22,2
65-70°	3,7	10,8	12,2	7,9	11,6
70-115°	22,0	8,4	14,8	11,8	13,2
115-120°	—	23,8	11,5	13,9	15,2
High-boiling residue	30,2	19,2	28,6	46,7	37,6

b.p. 35.0-35.5°; d_4^{20} 0.6300 and n_D^{20} 1.3608; III) b.p. 87-90°, d_4^{20} 0.6889 and n_D^{20} 1.3900. We obtained similar products in experiments over alumina. The Raman spectra confirmed that I is isopentane, II n-pentane, and III 2-methylhexane [2]. The last hydrocarbon is undoubtedly a product of addition of two molecules of ethylene to propane.

It follows from Fig. 2 that the yield of the expected heptane fraction when n-butane is alkylated with ethylene over calcium phosphate is higher than that obtained over quartz. The optimum temperature is 450°. The fractionation curve of the alkylate from expt. 9 is plotted in Fig. 2. After unsaturateds had been removed from the fraction with b.p. 60-65° (bromine number 5), it had the following constants: b.p. 62-63°, d_4^{20} 0.6646, n_D^{20} 1.3768. The Raman spectrum of a fraction with similar properties obtained over alumina had frequencies characteristic of 3-methylpentane [3]. On the fractional distillation curve of the catalyzate, this fraction corresponds to portion 1. A 115-118° fraction (d_4^{20} 0.7100, n_D^{20} 1.4005) corresponds to portion 2. These properties are identical with those of 3-methylheptane — the product of addition of two molecules of ethylene to n-butane [3]. Among the gaseous products of expt. 12 (at 500°) were detected only small quantities of H_2 , CH_4 , and C_2H_6 . The weight increase of the catalyst after the experiment (duration 2.5 hr) was 5%. This points to a very weak cracking reaction over calcium phosphate.

Alkylation of n-hexane with ethylene. The experiment was carried out over phosphate P at 450° and 450 atm. The reaction mixture contained 16 wt.-% of ethylene, and the space velocity of the mixture was 2.3. The yield of alkylate was 143%. The yield of octane fraction with b.p. 115-120° (bromine number 23) was 23.2%. Chromatography on silica gel gave a saturated hydrocarbon with b.p. 117°, d_4^{20} 0.7106, n_D^{20} 1.4002. The following frequencies were found ($\Delta \nu$) in cm^{-1} in its Raman spectrum: 298(1), 315 (broad); 821(1); 874(2); 895(3); 908(1); 961(broad); 978(1); 99(0); 1040(2); 1064(2) diffuse; 1083(1); 1147 (2); 1167(2); 1302(3); 1444(10); 1464(10). These are characteristic of 3-methylheptane. Literature data for 3 methylheptane [4]: b.p. 118.93°, d_4^{20} 0.7058, n_D^{20} 1.3985.

Alkylation of isopentane by ethylene. The reaction was carried out over phosphate P at 450° and 450 atm. The mixture contained 17.3 wt.-% of ethylene. The space velocity was 2.4, and the yield of alkylate 183%. The expected isoeptane fraction (86-92°) was obtained in a yield of only 12.7 wt.-%. Its bromine number was 28. The nonane fraction (130-140°) was the product of addition of two molecules of ethylene to isopentane (yield 9.1%). The 30-86° fraction amounted to 26% and was a product of cracking. Its bromine number was 46. Under similar conditions over alumina an alkylate containing 23% of isoeptane fraction was obtained [2].

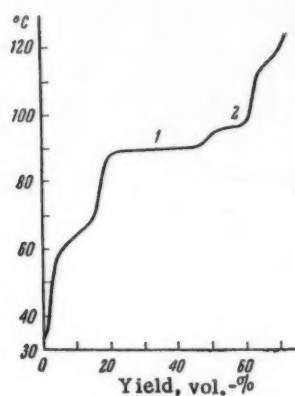


Fig. 3.

Alkylation of n-butane by propylene, butylene, and isobutylene. Results of experiments with propylene are set forth in Table 3, those with n-butylene and isobutylene in Table 4. It follows from Table 3 that in alkylation of n-butane by propylene over phosphate P the highest yield of the expected heptane fraction is obtained at 500° and 450 atm. We see from the alkylate fractionation curve (Fig. 3) that the main bulk of the heptane fraction (about 80%) came over at 89.5-90.5°; a smaller fraction came over at 96-97°. The 86-92° fraction (bromine number 13) was chromatographed and then had d_4^{20} 0.6899 and n_D^{20} 1.3897. As was shown earlier [1], a fraction with similar constants consisted mainly of 3-methylhexane. It follows from Table 4 that the reactions of n-butane with n-butylene and isobutylene give very much lower yields of alkylate and of the anticipated octane fraction. The alkylation products were accompanied by a considerable amount of unsaturated hydro-

carbons — products of dimerization of the initial olefins. Figure 4 contains fractionation curves of alkylates of expt. 21 (curve 1) and expt. 25 (curve 2). The main bulk of the octane fraction is seen to come over at 103-110°. After removal of unsaturateds it had b.p. 106-107°, d_4^{20} 0.7177, n_D^{20} 1.4018. Its Raman spectrum contained the following frequencies ($\Delta \nu$) in cm^{-1} : 315(1); 770(1); 827(2); 907(1); 955(3); 996(2); 1032(1); 1048(1); 1152(2); 1169(1 broad); 1237(0); 1309(0); 1353(2); 1465(7 broad), which are characteristic of 2,4-dimethylhexane. Literature data for 2,4-dimethylhexane: b.p. 109.4°, d_4^{20} 0.7004, n_D^{20} 1.3953. The spectrum of this fraction also contains frequencies characteristic of a cyclane which could not be identified with certainty. This impurity may be responsible for the low values of d_4^{20} and n_D^{20} of 2,4-dimethylhexane.

TABLE 3

Experimental conditions and composition of alkylate	Experiment number	
	17	18
Temperature, °C	450	500
Pressure, atm	450	450
Butane: propylene, by volume	4,9	5,6
Space velocity	940	960
Degree of ethylene conversion, %	37	60
Yield of alkylate, weight-%	63	90
Yield of fractions, weight-%		
up to 70°	13,1	14,8
70-92°	21,1	36,2
92-100°	15,3	8,6
100-125°	10,6	11,5
High-boiling residue	40,0	29,0

TABLE 4. Phosphate as Catalyst

Experimental conditions and composition of alkylate	Butylene	Isobutylene			
		experiment number			
	19*	21	22	24	
Temperature, °C	450	450	450	400	
Pressure, atm	500	500	500	450	
Butane: olefin, by volume	6	7,3	4,5	5,2	
Space velocity	930	920	900	1800	
Degree of olefin conversion, %	40	50	50	44	
Yield of alkylate, weight-%	26	48	48	36	
Yield of fractions, weight-%					
60-100°	12,4	9,3	9,7	6,0	
100-110°	3,3	43,9	31,1	41,5	
110-120°	43,2	14,3	19,7	12,0	
High-boiling residue	41,1	32,1	37,4	40,5	
Content of unsaturated hydrocarbons in 100-110° fraction, calculated on octenes, weight-%	39*	45	50	95	

*For 110-120° fraction.

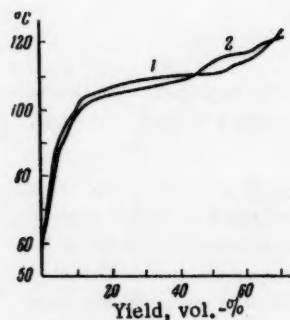


Fig. 4.

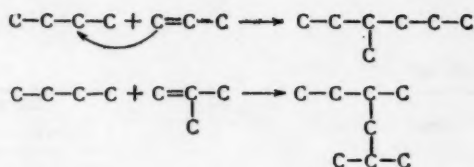
Evaluation of Results

Results of the present work, taken in conjunction with preceding investigations, enable us to compare the course of alkylation under similar conditions in presence of calcium phosphate, alumina, and crushed quartz. We see that calcium phosphate and alumina do not catalyze the alkylation of propane with ethylene and even retard it. Thus the yield of pentane fraction at 450° and 450 atm was 8% in presence of alumina, 15.8% in presence of phosphate, 33.4% in the presence of calcium phosphate, and 45% over quartz. On the other hand in the alkylation of n-butane with ethylene at 450° and 450 atm the yield of hexane fraction was 47.2% over calcium phosphate, 37.3% over alumina, and 33.8% over quartz. The catalytic effect of calcium phosphate (as well as of alumina) is still more marked in the alkylation of n-butane with propylene. The yield of heptane fraction over phosphate at 450° and 450 atm was 36.3%, and at 500° and 450 atm it was 44.8%. Over alumina the yields were respectively 30 and 28%, while over porcelain crocks it was 13.4%.

The yield of the expected fraction decreases with increasing molecular weight of the paraffin. In the reaction of n-hexane with ethylene, for example, the yield of octane fraction is 23%. Branching of the paraffin molecule

lowers the yield of the expected fraction still further. Only 14.8% of isoheptane fraction is present in the alkylate after alkylation of isopentane with ethylene at 450° and 450 atm over phosphate. The yield of alkylate decreases with increasing molecular weight of the olefin (ethylene – butylenes) and the proportion of unsaturateds increases. The products of alkylation of n-butane with butylene and isobutylene contained 53 and 41% of octenes respectively. This indicates an increasingly important role of simultaneous secondary reactions. Smaller amounts of high-boiling residual products, carbonaceous deposits, and cracked substances are generally formed over phosphate catalyst than over alumina. Analysis of the products of alkylation shows that although alumina and calcium phosphate are capable of raising the yield of the expected hydrocarbons, they do not change the direction of alkylation in comparison with the thermal reaction.

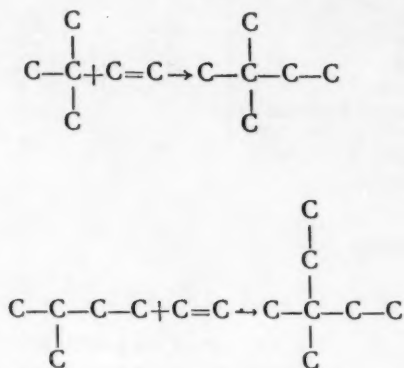
The present work brings additional experimental confirmation of the hypothesis of a free-radical mechanism of the alkylation of paraffins with olefins [5]. This approach provides an explanation of the structure of the resulting hydrocarbons. It has been shown by a number of investigators [5-7] and by us [8] that in alkylation of normal paraffins the olefin combines at its least unsaturated carbon atom preferentially with the secondary carbon atom of the paraffin:



Addition at the primary carbon atom takes place to a very much smaller extent:

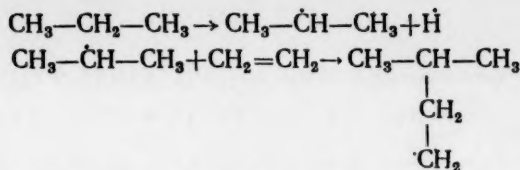


In the alkylation of isoparaffins the olefin combines predominantly at the tertiary carbon atom:

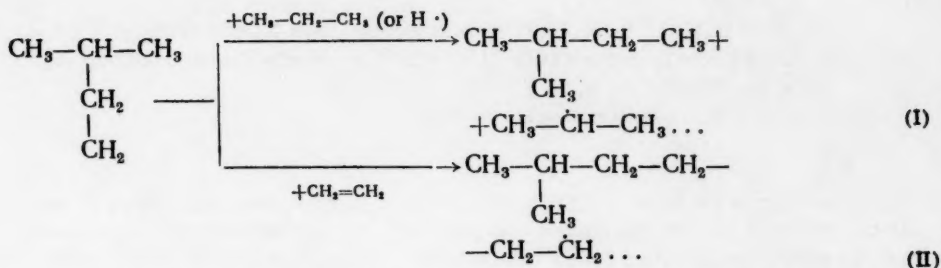


The differences in the direction of alkylation of normal and branched paraffins are readily explained by differences in the ease of formation of primary, secondary, and tertiary alkyl radicals. It is known that a tertiary radical is formed most easily and a primary radical least easily.

Additional confirmation of the radical mechanism is forthcoming from a study of the structure of the products of addition of two and more molecules of olefin to a paraffin. For the first time we isolated and characterized such products in reactions of propane and n-butane with ethylene. It was found that the second molecule of olefin combines not at the tertiary (or secondary) carbon but at the primary carbon atom of the unbranched end of the isoparaffin molecule. The product of addition of two molecules of ethylene to a molecule of propane, for example, was 2-methylhexane, while the corresponding product of addition to n-butane was 3-methylheptane. Addition of two molecules of ethylene to isobutane gives 2,2-dimethylhexane [9], while isopentane and two molecules of ethylene give 3,3-dimethylheptane [2]. Formation of these hydrocarbons is easily explained by the following radical mechanism:



The resulting isoamyl radical can probably interact in two directions:



In the former case a stable hydrocarbon molecule is formed, and in the latter a radical which can build up the chain to the stage of formation of products of addition of three and more molecules of olefin which are also attached to the primary but not to the secondary or tertiary C atoms. In earlier work [6, 7, 10] the radical mechanism of alkylation was supported by the observation that the process was accelerated by introduction of radical-formers (alkyl halides) into the reaction sphere.

The authors express their gratitude to N. I. Ershov for his participation in the discussion of the work, and to G. K. Gaivoronskaya for plotting and identifying the Raman spectra.

SUMMARY

1. The alkylation of paraffinic hydrocarbons (C_3 - C_6) with olefins (C_2 - C_4) at high temperatures and pressures was investigated.
2. Alkylation can proceed thermocatalytically over calcium phosphate and alumina.
3. The first molecule of olefin joins on at the secondary C atom of a normal paraffin or to the tertiary C atom of an isoparaffin. The second molecule of olefin combines only at the primary C atom of the resulting isoparaffin. Such a difference in the mode of addition of the first and second molecules of olefin is explained in terms of a radical mechanism of the process.
4. Increasing molecular weight of paraffins and olefins is accompanied by decreasing alkylation reactivity.

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THE KINETICS OF THE HYDROGENATION OF THE VINYL ETHER
OF β -(DIETHYLAMINO)-ETHANOL AND OF VINYL PHENYL ETHER
ON 1%-Pd/Al₂O₃

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The study of the kinetics of the hydrogenation of compounds having radicals of various structures attached to the double bond is of considerable interest both practically and scientifically since it allows one to penetrate more deeply into the phenomena occurring during hydrogenation. The work of Golodov and Sokol'skii [1] is interesting in this connection; they investigated in a rather detailed way the kinetics of the hydrogenation of vinyl ethyl ether, vinyl isopropyl ether, vinyl butyl ether, vinyl phenyl ether, the monovinyl ether of ethylene glycol, and the vinyl ether of monoethylamine in a medium of 96% alcohol and 0.1 M NaOH. Skeletal nickel, Pd/CaCO₃, and in several cases Pt-black were the catalysts used. The authors showed that with increased length of the chain of the radical ($H_2C = CH-OR$), and also with its branching, the rate of the reaction decreased. The introduction of the amino group rather interestingly affects the kinetics of the hydrogenation. It follows from the data of the authors that the relative rates of the hydrogenation reaction for vinyl phenyl ether and the vinyl ether of monoethanolamine very strongly depend on the medium and on the nature of the catalyst. In alcohol this ratio is greater than unity, whereas in an alkaline medium it is substantially less than unity. It appeared interesting to investigate in a comparative manner the kinetics of the hydrogenation of vinyl phenyl ether and of an ether which had a diethyl-substituted amino group. As the subject for the investigation of a compound containing the radical $-N(C_2H_5)_2$, we selected the vinyl ether of β -(diethylamino)-ethanol. In agreement with the data in the literature [2], this ether was easily hydrogenated; the kinetics of its hydrogenation have not been studied to this time. The investigation was carried out in diisopropyl ether solution. Aluminum oxide containing 1% palladium was the catalyst used.

EXPERIMENTAL PART

The catalyst was prepared by impregnating powdered aluminum oxide [3] with the calculated quantity of a solution of H_2PdCl_4 . The catalyst was reduced in a stream of electrolytic hydrogen at 330° for 10 hrs. The specific surface of the catalyst based on the adsorption of benzene [4] was 142.5 m²/g. The most probable size of the particles according to sedimentation analysis was 12 microns. The ethers were purified by known methods [5] and possessed the following properties.

	b.p. in °C	n_D^{20}	d_4^{20}
Vinyl phenyl ether	46.1-46.3 (3 mm)	1.5220	0.9778
The vinyl ether of β -(diethylamino) ethanol	156-158	1.4333	0.8392
Diisopropyl ether	68.3-68.5	1.3685	0.7278

The experiments were carried out in a hydrogenation flask, to which was introduced an aliquot of the catalyst and 10 ml of diisopropyl ether; the catalyst was saturated with hydrogen at 20° for 15 min, and then an aliquot of the ether to be investigated was introduced. The rate of the reaction was determined by the absorption of hydrogen. Not less than 2-3 parallel experiments were carried out each time. The experiments were satisfactorily reproducible. The hydrogenation flask was shaken 600 times per min in all cases. Preliminary experiments had shown that under these conditions the best reproducibility was attained, and the rate of the reaction had practically ceased to depend on the rate of agitation.

Experiments carried out on the hydrogenation of vinyl phenyl ether over 0.50 g of the catalyst showed that the activity of the catalyst was practically unchanged for the sequential hydrogenation of up to 5 aliquots (0.40 g) of the

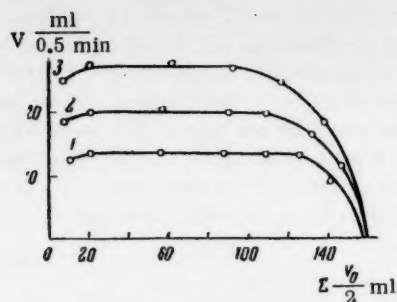


Fig. 1. The dependence of the rate of hydrogenation of vinyl phenyl ether on the temperature. The weight of the catalyst was 0.50 g: 1) Temperature 20°, 0.83 g of ether; 2) temperature 30°, 0.84 g of ether; 3) temperature 40°, 0.84 g of ether.

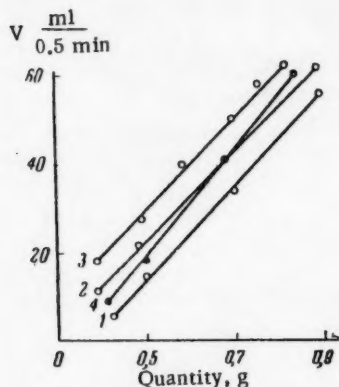


Fig. 3. The dependence of the rate of hydrogenation of ethers on the quantity of catalyst: 1) $\text{H}_2\text{C}=\text{CHOC}_6\text{H}_5$, temperature 20°; 2) $\text{H}_2\text{C}=\text{CHOC}_6\text{H}_5$, temperature 30°; 3) $\text{H}_2\text{C}=\text{CHOC}_6\text{H}_5$, temperature 40°; 4) $\text{H}_2\text{C}=\text{CH}-\text{OC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, temperature 20°.

we observed a considerable decrease of the rate of the process during the hydrogenation of a second aliquot of the ether on the same portion of catalyst. The hydrogenation was carried out in the presence of the product of the reaction of the first experiment. During the hydrogenation of the first aliquot (20°, 0.67 g) of the ether on 0.65 g of the catalyst, the rate of hydrogenation was equal to 37 ml/0.5 min, but for the second aliquot (0.65 g), the rate was 31 ml/0.5 min. A suggested explanation of this fact is that the hydrogenation of the starting material is inhibited by its product — the ethyl ether of β -(diethylamino)-ethanol. Actually, during the hydrogenation of 1.28 g of a 1:1 mixture of the vinyl and of the ethyl ethers of β -(diethylamino)-ethanol the observed initial rate of hydrogenation was 33 ml/0.5 min.

The results of experiments on the hydrogenation of the vinyl ether of β -(diethylamino)-ethanol at temperatures of 20, 30, and 40° are presented in Fig. 2. It can be seen that the hydrogenation is of zero order only for a small initial interval, and that this interval decreases with increase of the temperature. It is apparent from Fig. 2 that, as is the case with vinyl phenyl ether, the rate of hydrogenation of the vinyl ether of β -(diethylamino)-ethanol also increases by 1.5 times for an increase of temperature of 10°. The dependence of the rate of reaction on the amount

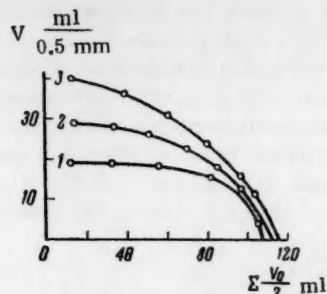


Fig. 2. The dependence of the rate of hydrogenation of the vinyl ether of β -(diethylamino)-ethanol on the temperature. The weight of the catalyst was 0.50 g: 1) Temperature 20°, 0.69 g of ether; 2) temperature 30°, 0.71 g of ether; 3) temperature 40°, 0.72 g of ether.

ether without removal of the reaction product. The rate of hydrogenation of the first aliquot was 14.1 ml/0.5 min, of the fifth aliquot 14.0 ml/0.5 min. The kinetic curves for the hydrogenation of vinyl phenyl ether at temperatures of 20, 30 and 40° are presented in Fig. 1. It is apparent from the curves of Fig. 1 that the reaction is of zero order, and that the rate of the reaction increases by approximately 1.5 times for a 10° rise of temperature. From the curves of Fig. 1 and of preliminary experiments, it is seen that the ethyl phenyl ether which is formed during the hydrogenation does not exhibit an inhibitory action on the hydrogenation process over the concentration range studied. From this, on the assumption that the hydrogenation of vinyl phenyl ether goes by an adsorption-desorption mechanism, one can conclude that the rate of the reaction is limited basically by the process of adsorption of the molecules of the substance being hydrogenated.

Some further results were obtained by us during the study of the hydrogenation of the vinyl ether of β -(diethylamino)-ethanol. During the hydrogenation of this substance

of catalyst, both for vinyl phenyl ether (curves 1, 2, 3) and for the vinyl ether of β -(diethylamino)-ethanol is shown in Fig. 3. As is apparent from the figure, we observed a linear dependence of the rate of reaction on the quantity of catalyst in all cases in the investigated concentration interval. It is also apparent from Fig. 3 that the curves of the dependence of the rate of hydrogenation of vinyl phenyl ether at the temperatures, 20, 30 and 40° were parallel within the experimental error. The curve showing the dependence of the initial rate of hydrogenation of the vinyl ether of β -(diethylamino)-ethanol on the quantity of catalyst had a somewhat different slope than those for vinyl phenyl ether. The conclusion may be drawn that the slope of the curve is determined by the nature of the substance being investigated. It is apparent from Fig. 3 that the initial rate of hydrogenation of the vinyl ether of β -(diethylamino)-ethanol is higher than the rate of hydrogenation of vinyl phenyl ether under the same experimental conditions.

SUMMARY

1. A comparative study of the kinetics of the hydrogenation in diisopropyl ether solution of the vinyl ether of β -(diethylamino)-ethanol and of vinyl phenyl ether was carried out over 1% Pd/Al₂O₃.
2. The 1% Pd/Al₂O₃ is an active catalyst for the hydrogenation of vinyl ethers.
3. The initial rate of the hydrogenation of the vinyl ether of β -(diethylamino)-ethanol is greater than the rate of hydrogenation of vinyl phenyl ether.

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AN INVESTIGATION OF THE PRODUCTS OF THE DEHYDROCYCLIZATION OF n-HEXANE AND OF THE DEHYDROGENATION OF CYCLOHEXANE OVER AN ALUMINUM-MOLYBDENUM CATALYST

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Although 25 years have passed since the discovery of the dehydrocyclization reaction of the paraffin hydrocarbons of various structures on both oxide [1, 2] and metallic [3] catalysts, nevertheless, investigations in this direction are continuing with great intensity. A broad literature [4-6] is devoted to the elucidation of the mechanism of the dehydrocyclization of hydrocarbons, to the experimental conditions, and to the preparation and action of various catalysts. At the present time in many countries catalytic plants are operating using oxide catalysts for the production of aromatic hydrocarbons and high octane gasoline.

From the literature relating to this question, it is apparent that the aromatic hydrocarbons obtained by the dehydrocyclization of alkanes over various oxide catalysts (Cr₂O₃-Al₂O₃, MoO₃-Al₂O₃, V₂O₅-Al₂O₃) contain the same number of carbon atoms as the original hydrocarbon. It is also known that aromatic hydrocarbons with a smaller number of carbon atoms than the original hydrocarbon are formed from high molecular weight paraffins. Apparently in the literature there is no data on the formation of aromatic hydrocarbons of higher molecular weights than the original paraffin.

During an investigation of the conditions of poisoning of an industrial aluminum-molybdenum catalyst when it was being used for the dehydrocyclization of pure n-hexane and for the dehydrogenation of pure cyclohexane, we noticed a very interesting fact. A study by the gas-liquid chromatographic method [7] of the liquid product of the catalysis showed that the catalyzate from normal hexane contained besides benzene and unconverted hexane several isomeric hexanes, n-pentane and isopentane. In addition, the catalyzate from the dehydrocyclization of n-hexane at 520° contained considerable quantities of toluene. With the help of the combination dispersion spectra, the aromatic part of the catalyzate from n-hexane was observed to contain small quantities of xylenes, ethylbenzene and other higher molecular weight aromatic hydrocarbons. Methylcyclopentane, cyclohexane, and isohexane were observed among the products of the reaction of cyclohexane in addition to benzene.

EXPERIMENTAL PART

All the experiments on the conversion of pure hydrocarbons were carried out in an ordinary catalytic apparatus of the flow-through type at atmospheric pressure in a stream of hydrogen. The dehydrogenation of cyclohexane was studied at 488°, the dehydrocyclization of n-hexane at 488 and 520°. The starting materials were introduced into the reaction tube at a volume rate of 0.2 hrs⁻¹ at a molar ratio of H₂: HC = 5. Before the start of each experiment a fresh portion of the industrial aluminum-molybdenum catalyst (approximately 17 ml) was heated at 500° in a stream of hydrogen for 6 hrs. During the experiment, at definite time intervals, samples of the catalyzate were removed from the receiver, and were subjected to analysis. The results of the experiments are given in Tables I and II.

TABLE 1. The Composition of the Product of the Catalysis of Cyclohexane on an Industrial Aluminum-Molybdenum Catalyst (c = 488°; v = 0.2 hrs⁻¹; H₂: HC = 5)

Reaction product	The composition of the catalyzate in weight percent after							
	1 hr.	2 hrs.	3 hrs.	5 hrs.	10 hrs.	20 hrs.	30 hrs.	45 hrs.
Benzene	63,0	56,4	53,4	47,0	37,1	29,4	25,8	21,8
Cyclohexane	34,5	41,0	44,2	50,4	60,2	68,4	71,8	75,7
Cyclohexene	0,4	0,4	0,5	0,4	0,3	0,3	0,4	0,5
Methylcyclopentane	1,5	1,6	1,4	1,4	1,5	1,6	1,5	1,5
Hexanes	0,6	0,6	0,5	0,8	0,9	0,3	0,5	0,5

TABLE 2. The Composition of the Product of the Catalysis of n-Hexane on an Industrial Aluminum-Molybdenum Catalyst at 488 and 520° (v = 0.2 hrs⁻¹; H₂: HC = 5)

Temp. of the expt., °C	Time of the expt., hrs.	Composition of the catalyzate in weight-%						
		benzene	toluene	n-hexane	2-methylpentane	3-methylpentane	i-C ₈	hexenes
488	1	19,3	—	67,4	5,4	4,8	3,1	—
	2	14,2	—	65,8	6,6	5,4	5,4	2,6
	5	10,5	—	69,4	7,3	6,1	4,1	2,6
	10	8,7	—	72,1	6,8	4,8	3,2	4,4
	12	6,2	—	64,4	7,7	6,3	8,4	3,0
520	1	43,8	15,3	34,6	1,9	1,6	1,0	1,8
	2	39,0	13,4	39,7	2,9	2,6	1,0	1,8
	5	26,6	8,7	57,5	2,3	2,1	1,0	1,8
	15	18,3	6,5	67,6	2,8	2,7	с.п.	1,2
	30	12,6	2,5	79,8	1,8	1,9	с.п.	1,4

The data obtained show that on an industrial aluminum-molybdenum catalyst, along with the dehydrogenation of the cyclohexane, there also proceed reactions of isomerization of the 6-membered ring into a 5-membered and of splitting of the naphthene hydrocarbon to alkanes of n- and iso-structures with the same number of carbon atoms in the molecule.

From the data of Table 1, it is apparent that the dehydrogenating activity of the aluminum-molybdenum catalyst gradually decreases during the experiment, and that after 45 hrs of use it has only 34,6% of the initial activity.

TABLE 3. Distillation of the Aromatic Part of the Catalyzate from n-Hexane

Fraction number	Boiling point, °C	Quantity, g
I	80-90	35,66
II	90-105	0,35
III	105-120	5,37
IV	120-150	4,00
V	Above 150	3,58
Losses		0,79

The following products were observed from the dehydrocyclization of n-hexane on the same catalyst under the same conditions: benzene, 2- and 3-methylpentanes, n-pentane, isopentane, and small quantities of hexene-1 and hexene-2. As is apparent from Table 2, at 488° the dehydrocyclizing activity of the aluminum-molybdenum catalyst even at the beginning of the experiment is only 19.3%, and after 12 hrs. of use it decreases to 6.2%. An increase of the temperature of the catalysis to 520° led to an increase of the initial activity of the catalyst by almost 2.5 times. However, under these conditions there was observed among the products of the reaction (in addition to those hydrocarbons innumera- rated above) a noticeable quantity of toluene, the amount of which reached 15.3% at the beginning of the experiment, although it

thereafter gradually decreased during 30 hours to 2.5%. In order to analyze more carefully the composition of the aromatic part of the catalyzate, the latter was subjected to chromatographic separation on silica gel. From 186.25 g of catalyzate were isolated 49.75 g of aromatic hydrocarbons, which then were fractionally distilled (Table III).

An analysis of these fractions with the help of the combination dispersion spectra showed that fraction 1 consisted completely of benzene, fraction 3 contained pure toluene, fraction 4 contained a mixture of ethylbenzene and m- and p-xylene, and that fraction 5 apparently was composed of a mixture of aromatic hydrocarbons with condensed nuclei.

SUMMARY

1. The constitution of the products of the catalysis of cyclohexane and n-hexane over an industrial aluminum-molybdenum catalyst was investigated at 488° and 520° respectively ($v = 0.2 \text{ hr}^{-1}$; $\text{H}_2 : \text{HC} = 5$).

2. In the catalyzate obtained at 520° from n-hexane over this catalyst there were observed noticeable quantities of aromatic hydrocarbons of greater molecular weight than the starting materials; the presence of these obviously depends on alkylation of the product benzene by the products of the hydrocracking of n-hexane.

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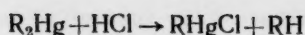
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A SERIES OF RADICALS, ARRANGED ACCORDING TO THE RATE OF THEIR REMOVAL FROM AN ATOM OF MERCURY BY HYDROCHLORIC ACID

A. N. Nesmeyanov, A. E. Borisov, I. S. Savel'eva and N. V. Kruglova

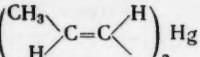
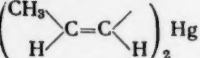
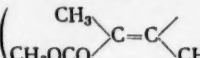
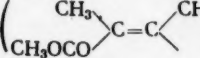
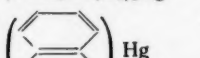
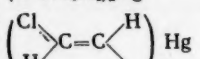
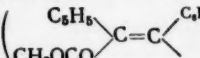
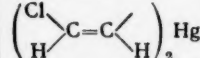
The Institute of Heteroorganic Compounds, Academy of Sciences USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 4, pp. 726-727, April, 1961
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The present article summarizes a series of rate constants for the acidolysis of mercury organic compounds according to the reaction



and also gives in several cases the activation energies of these reactions. A comparison with a broader list of radicals, and a comparison with the electronegativity series of Kharasch [1] will be made later. The rate constants of the reactions investigated and included in the table of substances were measured at molar concentrations of 0,005 M/l R_2Hg and 0,01 M/l HCl (1: 2) in dioxan-water solution (9: 1).

Reaction Rate Constants and Activation Energies

No. in order	Formula	Constants, l/M sec ⁻¹				Activation energy, cal/M
		15°	20°	30°	40°	
1	 Hg	11° 8,02 · 10 ⁻²	1,32 · 10 ⁻¹	2,21 · 10 ⁻¹		18750
2	 Hg	11° 6,81 · 10 ⁻²	1,09 · 10 ⁻¹	1,75 · 10 ⁻¹		17000
3	(p-CH ₃ OC ₆ H ₄) ₂ Hg			1,15 · 10 ⁻¹		
4	 Hg			5,48 · 10 ⁻²		
5	 Hg			4,60 · 10 ⁻²		
6	(o-CH ₃ C ₆ H ₄) ₂ Hg		1,08 · 10 ⁻²	4,50 · 10 ⁻²	1,71 · 10 ⁻¹	23200
7	(p-CH ₃ C ₆ H ₄) ₂ Hg			4,18 · 10 ⁻²	1,38 · 10 ⁻¹	
8	(o-CH ₃ OC ₆ H ₄) ₂ Hg		3,39 · 10 ⁻³	1,53 · 10 ⁻²		
9	 Hg	50° 1,54 · 10 ⁻¹		1,37 · 10 ⁻²	5,04 · 10 ⁻²	22450
10	(m-CH ₃ C ₆ H ₄) ₂ Hg			1,22 · 10 ⁻²		
11	(CH ₂ =CH) ₂ Hg		2,77 · 10 ⁻³	8,87 · 10 ⁻²	2,33 · 10 ⁻²	19400
12	(C ₆ H ₅) ₂ Hg		1,76 · 10 ⁻³	6,65 · 10 ⁻³	2,36 · 10 ⁻²	23600
13	(p-ClC ₆ H ₄) ₂ Hg	60° 4,87 · 10 ⁻¹		1,21 · 10 ⁻³	4,35 · 10 ⁻³	24800
		50°	60°	70°	80°	
14	(m-ClC ₆ H ₄) ₂ Hg		1,13 · 10 ⁻²	3,62 · 10 ⁻²		
15	 Hg		1,04 · 10 ⁻²	3,16 · 10 ⁻²		
16	 Hg	3,42 · 10 ⁻³		2,86 · 10 ⁻²	8,44 · 10 ⁻²	24100
17	 Hg		5,87 · 10 ⁻³	1,31 · 10 ⁻²		
18	(o-ClC ₆ H ₄) ₂ Hg	7,51 · 10 ⁻⁴	1,86 · 10 ⁻³			

The measurement of the kinetics of the reactions. A 100 ml volumetric flask containing a solution of an aliquot of R_2Hg (0,005 M/l) in 75-85 ml of dioxan (not containing peroxide) was maintained in a thermostat at a given temperature for 25-30 min; in separate flasks in the thermostat were 10 ml of 0,1 N hydrochloric acid and 5-15 ml of dioxan. The 10 ml of acid was then rapidly added to the R_2Hg solution, the flask was washed out several times with dioxan into the acidified R_2Hg solution, and the solution volume was brought to the mark with dioxan. The mixture was rapidly shaken and a 10 ml sample was removed. The mixing and the removal of the first sample required 2-3 min. The moment of mixing of the reagent was taken as the initial reading for the term of the reaction.

The sample taken was poured into twice its volume of ice-cold distilled water (not containing carbon dioxide), and was titrated with 0.01 NaOH in the presence of Methyl Red. An equal amount of the acid was titrated separately as a control. Reactions were carried out at temperatures from 11-80°. Samples were removed after 3, 5, 8, 10, 20, 30, 40, etc. min, depending on the rate of the reaction.

SUMMARY

A series of rate constants for the acidolysis of mercury organic compounds by HCl is given, as is also the activation energy of several of these reactions.

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THE CARBOCYCLIZATION OF 1,6-ANHYDROGALACTOSES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
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Original article submitted September 17, 1960

The carbocyclization reaction of 1,6-anhydroglucopyranoses was first realized in 1939 by Shorygin and Makarova-Zemlyanskaya (Shorygina) [1]. Phenol was obtained by them in 34% yield by the action of metallic sodium on the trimethyl ether of levoglucosan in a liquid ammonia medium.

In 1957 we published a communication [2] on the results of a further investigation of this interesting reaction. The yield of phenol was raised to 60% by changing the conditions for the isolation of the reaction product. The influences of temperature, ratio of the quantities of trimethyl-levoglucosan and of metallic sodium, and the time of interaction on the yield of phenol were also shown. The optimum conditions for the reaction were established. The presence of resorcinol and pyrocatechol in addition to phenol in the products of reaction was established with the help of paper chromatography.

For the purpose of investigating the specificity of the reaction we have carried out the reaction of 1,6-anhydrogalactopyranose with metallic sodium in liquid ammonia under the optimum conditions which we had found for the trimethyl ether of levoglucosan. It was found that the reaction proceeded with the formation of phenol in 27% yield. The work is continuing.

EXPERIMENTAL PART

2,3,4-Tri-O-methyl-1,6-anhydrogalactopyranose, 1,6-anhydrogalactopyranose (I) [3]. A 65 g aliquot of lactose was subjected to pyrolysis at 20 mm over a gas flame. The aqueous distillate was clarified and was concentrated in vacuo to a syrup. A solution of the syrup in acetone was shaken with anhydrous copper sulfate. After removal of the acetone, the crude product was worked up with chloroform. From the chloroform extract, after removal of the solvent, there was isolated crystalline 3,4-O-methylene-1,6-anhydrogalactopyranose, m.p. 151° (from ethyl acetate). By the action of 0.1 M sulfuric acid (100 ml) on 6.5 g of this material for 24 hrs. at room temperature, there was obtained 1,6-anhydrogalactopyranose which was isolated after neutralization of the solution with barium carbonate and concentration of the filtrate in vacuo. Recrystallization from alcohol gave 3.46 g of product, m.p. 224°.

2,3,4-Tri-O-methyl-6-anhydrogalactopyranose (II). (I) 3.46 g. was methylated with 13.8 ml of dimethyl sulfate and 13.72 g of sodium hydroxide in 24 ml of water. The methylation was repeated under the same conditions. The trimethylether (3 g) was isolated with chloroform and recrystallized from a mixture of acetone and petroleum ether, m.p. 60°.

The interaction of 2,3,4-Tri-O-methyl-1,6-anhydrogalactopyranose with metallic sodium in liquid ammonia.

A 0.7 g sample of (II) was dissolved in 15 ml of liquid ammonia in a glass ampoule, and to this was added 0.5 g of metallic sodium. The reaction mixture was kept in the sealed ampoule for 10 hrs at the temperature of dry ice and thereafter for 48 hrs at room temperature with periodic shaking; the blue color of the solution completely disappeared. After removal of the ammonia, the residue was decomposed with water and acidified with sulfuric acid; the phenol was removed by steam distillation.

The yield of phenol was determined according to Koppeshaar and amounted to 26%. In an analogous experiment the yield of phenol reached 27.9%.

SUMMARY

2,3,4-Tri-O-methyl-1,6-anhydrogalactopyranose, like 2,3,4-Tri-O-methyl-1,6-anhydroglucopyranose forms phenol by the action of a solution of metallic sodium in liquid ammonia.

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LETTERS TO THE EDITOR

ON THE NATURE OF THE FERMENTATIVE ACTIVITY OF LYSOZYME

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Translated from *Izvestiya Akademii Nauk, SSSR, Otdelenie Khimicheskikh Nauk*,
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Original article submitted February 24, 1961

When native lysozyme reacts with iodoacetic acid at pH 5.5 and a temperature of 40° for six hours, a modification of the lysozyme molecule occurs owing to the addition of acetic acid residues. As a matter of fact, on chromatographing the reaction mixture on Amberlite resin CG-50, all the protein, basically, is divided into two peaks: one corresponding to the original lysozyme and the other corresponding to a more acid protein which is eluted from the resin somewhat sooner.

A test of the lytic ability on *Micrococcus lysodeikticus* showed that the more acid protein possesses fermentative activity that is even somewhat greater (by 12-13%) than that of the original native lysozyme.

A study of the amino acids of this modified lysozyme (quantitative chromatographic analysis on Amberlite CG-120 ion-exchange resin) showed that, in contrast to the original lysozyme, histidine is absent from this protein, but it contains another amino acid which, according to the data in the literature, was determined to be 1 (or 3)-carboxymethylhistidine.

Thus, as a result of the reactions of lysozyme with iodoacetic acid under the conditions mentioned, N-carboxymethylation of the imidazole ring of histidine occurs and the resulting modified lysozyme with blocked histidine does not lose its fermentative activity.

The discovery of this phenomenon permits us to assume, with a considerable degree of probability, that the single histidine residue in the molecule is not part of the active center of fermentation.

THE INFLUENCE OF THE SOLVENT ON THE SPATIAL DIRECTIVITY OF THE WITTIG REACTION

L. D. Bergel'son, V. A. Vaver and M. M. Shemyakin

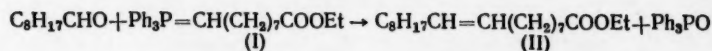
The Institute of the Chemistry of Natural Compounds, Academy of Sciences USSR

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Original article submitted March 1, 1961

It is known that the Wittig reaction leads to mixtures of stereoisomeric olefins, in which the trans forms usually predominate [1]. We have established that by carrying out the Wittig reaction in dimethylformamide in the cold, the ratio of the stereoisomeric products of the reaction changes; a greater proportion of the cis-isomer are formed. Thus, by the condensation of benzylidene-triphenylphosphorane with benzaldehyde in dimethylformamide, we obtained a mixture of cis- and trans-stilbenes in a 75: 25 ratio; when the same reaction is carried out in ether [2], the ratio of cis- to trans-isomers is 30: 70. The condensation of triphenyl- ω -carbyethoxyoctylidene phosphorane (I) with pelargonic aldehyde by the method worked out by us [3] in tetrahydrofuran leads to the unsaturated ester (II), the hydrolysis product of which judging by the infra-red spectra [4] consists of a mixture of the cis- and trans-acids in a 3: 1 ratio. In dimethylformamide the reaction becomes stereospecific and leads to a product which contains about 95% oleic acid.



The possibility of regulating the steric directivity of the Wittig reaction by means of the selection of a suitable solvent has been discovered.

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COMPOUNDS OF THE TYPE $(RCH = CR')_3Sb(C_2H_5)_2$

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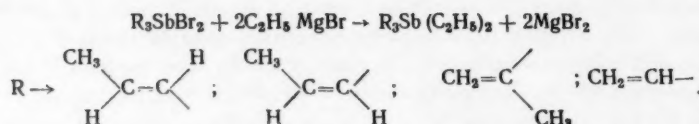
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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Original article submitted March 13, 1961

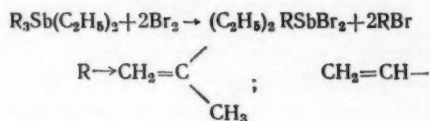
We have described the synthesis of the cis- and trans-isomers of propenyl [1] and vinyl compounds of tri- and pentavalent antimony [2]. Continuing our investigations of this field of the chemistry of the metal-organic compounds we are now able to discuss the synthesis of antimony compounds of the type $(RCH = CR')_3Sb(C_2H_5)_2$.

The dibromides of tri-cis and tri-trans-propenylstibine, of triisopropenylstibine and of trivinylstibine smoothly react in an ether-tetrahydrofuran medium with ethyl magnesium bromide according to the scheme:



In this way are formed: diethyltri-trans-propenylantimony n^{20}_D 1.5395, d^{20}_4 1.2535, diethyltriisopropenylantimony n^{20}_D 1.5414; d^{20}_4 1.2008, diethyltrivinylantimony n^{20}_D 1.5470; d^{20}_4 1.2825, and diethyldi-cis-propenylstibonium hydroxide. Found: C 43.41; H 7.80%. Calculated for $C_{10}H_{21}Sb$: C 43.04; H 7.59%.

The reaction of diethyltriisopropenylantimony with 2 moles of bromine in chloroform led to the dibromide of diethylisopropenylantimony n^{20}_D 1.6155. Diethyltrivinylantimony behaves analogously, giving the dibromide of diethylvinylantimony n^{20}_D 1.6290.



Thus bromide splits off alkenyl groups.

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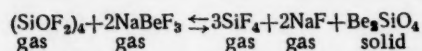
THE GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES
OF THE ACADEMY OF SCIENCES OF THE SSSR, NOVEMBER 24-25, 1960

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,
No. 4, pp. 731-732, April, 1961

At the general meeting of the Division which was held on the 24th and 25th of November, 1960, a report was given by member-correspondent of the AN SSSR A. V. Novoselova on the "Role of Transport Reactions in the Formation of Some Silicates." The speaker reported that at the present time numerous reactions are known by which one can realize the transfer of difficultly volatile substances from a hotter zone to a cooler and vice versa. Sheffer has called those reactions "transport" reactions which are realized as a result of the displacement of suitable heterogeneous equilibria if they are created by a temperature gradient. They are basic to important contemporary technological processes for the winning of metals of high purity, and undoubtedly have played an important role in the processes of mineral formation. Through the use of transport reactions, there has been obtained for the first time in the laboratory (by the speaker) monocrystals of phenacite, BeSiO_4 , willemite, Zn_2SiO_4 and their solid solutions. Obviously the mechanism of this process is a model of the indigenous formation of these silicates in nature.

The synthesis of phenacite occurred by heating a mixture of pure BeO and SiO_2 . Various additives were used as mineralizers; the best results were obtained in the presence of the beryllium fluorides of the alkali metals. For the synthesis of willemite, lithium zinc fluoride was added as the mineralizator to a mixture of zinc oxide and silicon dioxide. The reactions were carried out in evacuated sealed quartz ampoules at 800-1000°. Well-formed crystals of the silicate were found in the cooler part of the ampoule.

The formation of crystals of phenacite and willemite was observed to be several centimeters from the initial mixture of oxides, and obviously could occur only from the gas phase as a result of a "transport reaction." Apparently silicon fluoride is the carrier of oxygen and silicon in this reaction, and beryllium fluoride is the carrier of the beryllium. An investigation of the vapor pressure of sodium beryllium fluoride showed that in the gas phase there is actually present a complex molecule of beryllium fluoride. The formation of phenacite can occur as a result of the following reaction.



The formation of willemite obviously occurs in an analogous way.

Dr. of Chemical Sciences, Y. I. Mikheeva (co-author M. E. Kost) reported on the subject "The Hydrides of the Rare Earth Metals." The speaker pointed out that at the present time new data has been obtained which characterize the ratio of hydrogen to the majority of the rare earth metals, and which one can examine by a study of the hydrides of cerium - the rare earth metal most available in pure form. Pure cerium reacts with hydrogen without an induction period and with considerable evolution of heat. The maximum absorption at room temperature corresponds to the formula $\text{CeH}_{3.14}$. In the region $\text{Ce}-\text{CeH}_2$ a mechanical mixture of cerium and the dihydride is observed, while in the region $\text{CeH}_2-\text{CeH}_{3.14}$ there is but a single phase.

The pyrophoric hydride CeH_3 is decomposed at 300-400°, while the hydride CeH_2 is one of the most stable hydrogen compounds: even at 1050°, its melting point, dissociation is not complete. Lanthanum, samarium and gadolinium also energetically interact with hydrogen with the formation of the hydrides MeH_2 and MeH_3 . In the system lanthanum-hydrogen, there are regularities in the changes of properties of the hydride phase similar to those of the cerium-hydrogen system. Together with the general features of the behavior of the individual rare earth metals with relation to hydrogen, their individual properties are in evidence. In connection with this, it becomes especially interesting to study the properties of those hydride phases of variable composition as a function of the proportion of the rare earth metal.

Academician I. L. Knunyants reported on the subject "The Coupling of Bonds and New Rearrangements of the Perfluoroolefins." The speaker said that the fluoroolefins are strongly coupled systems since the polarization of the

carbon atoms is opposite to that of ordinary olefins. The coupling of the bonds of the fluoroolefins is most clearly apparent in their reactions with nucleophilic reagents; these are often accompanied by the substitution of the atoms of fluorine and by the rearrangement of the initial products. Thus, by the action of nucleophilic reagents on fluoroolefins, there are isolated, together with the product of addition, products which appear as a result of the substitution of fluorine atoms into allyl and vinyl positions. The author observed numerous cases of vinyl substitution by the action of alcohols, amines, phosphites, azides, hydroxylamine and other nucleophilic reagents on fluoroolefins. Vinyl substitution in many cases is apparently a result of the formation of a 4-membered, and sometimes even a 5-membered transition complex. The product of the vinyl substitution often rearranges to form the compound with the longest system of conjugated bonds. Thus, perfluoroallyl alkyl ethers rearrange into perfluoropropenyl alkyl, and tertiary perfluorovinylcarbinols into fluoroanhydrides of α -fluorocrotonic acid. Coupling of the bonds is strongly indicated even in the decomposition of the φ -azides. Thermal decomposition of the latter leads to new rearrangements of the saturated azides — into carbylamine fluorides, and of the unsaturated into new 4-membered systems. The coupling of the bonds is clearly apparent also in the decomposition of the salts of φ -carboxylic acids, of nitro- φ -carboxylic acids, in the stability of difluoronitroacetic acid, in the order of addition of nucleophilic reagents to substituted* acrylic acids, and in a series of other cases.

Member-correspondent of the AN SSSR D. N. Kursanov (co-author Z. N. Parnes) reported on the subject "New Data on Reactions of Hydride Displacement." The author reminded the audience that in organic chemistry reactions which include intermolecular or intramolecular transfer of a proton are broadly distributed and have been carefully studied. However, these reactions are not the only possible methods for the transfer of hydrogen. In particular, it is possible to transfer the hydrogen nucleus together with its electron cloud intermolecularly or intramolecularly. It is customary to call these reactions, reactions of hydride exchange or transfer. The possibility of reactions of hydride displacement is connected with the rather large affinity of the hydrogen atom for the electron, (17.6 kcal). The conception of hydride exchange is often utilized for the interpretation of the mechanisms of complex reactions. To these, for example, belong the Meerwein-Ponndorff reaction, the Tishchenko reaction, the Cannizzaro reaction, the reaction of isotopic exchange of hydrogen by saturated hydrocarbons, and others. However in these cases, the hydrogen exchange step is often only probable, and is not established with certainty. This depends to a considerable degree on the fact that the hydride exchanges, as a rule, are performed to carbonium ions, and are accompanied by the formation of a new carbonium ion; this is difficult to prove in the majority of cases.

For the study of the hydride exchange reaction, the author utilized cycloheptatriene as the donor of the hydride ion and tropiline as its acceptor. The formation of tropiline in reactions with cycloheptatriene and of tropene cycloheptatriene in reactions with tropiline simply show hydride exchange. A reversible reaction of hydride exchange was found between cycloheptatriene and tropiline. By the interaction of monodeuterocycloheptatriene with tropene the deuterium was distributed equally between the cycloheptatriene and the tropiline. This reaction, as was remarked by the author, is the first case in organic chemistry of a reaction of isotopic exchange of hydrogen dependent on a reversible hydride displacement. One can carry out this reaction in an acid medium (that is in the presence of protons), which shows that the reaction of hydride exchange proceeds through an activated complex and not through the formation of a free hydride ion. Using the tropilium ion as the acceptor of hydride ion, the speaker studied the hydride exchange reaction taking benzyl alcohol and ditropilyl ether as donors of the hydride ions. The hydride displacement reaction was studied with cycloheptatriene as the hydride ion donor and with aldehydes, ketones, nitriles, carboxylic acids, and their esters as the acceptors.

* Metforilakrilovye, in the Russian, a substituted acrylic acid whose nature is not clear—Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN
AĖ	Atomnaya ėnergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1955
Astr.(on). zh(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1959
Avto(mat). svarka	Astronomicheskii zhurnal	Soviet Astronomy-AJ	American Institute of Physics	34 1957
	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)	1 1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27 1956
	Biofizika	Biophysics	National Institutes of Health*	1 1957
	Biokhimiya	Biochemistry	Consultants Bureau	21 1956
Byull. ėksp(erim). biol. i med.	Byulleten' ėksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1959
DAN (SSSR)	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:	American Institute of Biological Sciences	106 1956
Dokl(adu) AN SSSR		Doklady Biochemistry Section	American Institute of Biological Sciences	112 1957
		Doklady Biological Sciences Sections (includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)		
		Doklady Botanical Sciences Sections (includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112 1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112 1957
		Doklady Earth Sciences Sections (includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124 1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-1 1957-1959
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	123 6 1958
		Doklady Soviet Mathematics	Consultants Bureau	123 6 1958
		Soviet Physics-Doklady (includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	The American Mathematics Society	131 1 1961
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)		
		Wood Processing Industry	American Institute of Physics	106 1 1956
		Telecommunications		
		Entomological Review	Consultants Bureau	106-1 1956-1957
		Pharmacology and Toxicology	Timber Development Association (London)	9 1959
		Physics of Metals and Metallurgy	Massachusetts Institute of Technology*	1 1957
		Sachenov Physiological Journal USSR	American Institute of Biological Sciences	38 1 1959
		Plant Physiology	Consultants Bureau	20 1 1957
		Geochemistry	Acta Metallurgica*	5 1 1957
		Soviet Physics-Solid State	National Institutes of Health*	1 1957
		Measurement Techniques	American Institute of Biological Sciences	4 1 1957
		Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences	The Geochemical Society	1 1 1958
			American Institute of Physics	1 1 1959
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952
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Ėntom(ol). oboz(renie) Farmakol. (i) toksikol(ogiya)	Ėntomologicheskoe obozrenie Farmakologiya i toksikologiya	Entomological Review Pharmacology and Toxicology	Consultants Bureau	106-1 1956-1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallurgy	Massachusetts Institute of Technology*	9 1959
Fiziol. zhurn. SSSR (im. Sichenova)	Fiziologicheskii zhurnal im. I. M. Sichenova	Sachenov Physiological Journal USSR	American Institute of Biological Sciences	38 1 1959
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	Consultants Bureau	20 1 1957
FTT	Geokhimiya	Geochemistry	Acta Metallurgica*	5 1 1957
Izmerit. tekhnika)	Fizika tvrdogo tela	Soviet Physics-Solid State	National Institutes of Health*	1 1957
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			American Institute of Physics	1 1 1958
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952

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